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# Elemental composition of concentrated brines in subduction zones and the deep continental crust

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## Abstract

It has been well established that fluids played an important part in determining chemical characteristics in many crustal terranes. Studies of fluid inclusions in eclogites have established that brines coexisted with the primary mineral assemblages during their metamorphic crystallization. These brines are currently multiply saturated in halide salts, carbonates, oxides, and sulfides. As a first step in quantitatively bounding the composition of the brines during metamorphism, the equilibrium compositions of the brines at room temperature were computed using the aqueous speciation codes EQ3/6. The results demonstrate that the brines are high density solutions (ca. 1.4 g/cm<sup>3</sup>) that have ionic strengths of approximately 8 mol, and are approximately 40% dissolved solids, by weight. These are predominately Na- and K-rich brines, with subordinate Ca and Mg. The approximate Na:K:Ca:Mg molar ratios are 4:2:0.5:0.2, but are sensitive to the assumed HCO<sub>3</sub><sup>-</sup> concentrations. Charge balance is primarily maintained by the very high Cl concentrations. These brines bear resemblance to brines analyzed from fluid inclusions in metamorphic rocks reported by Roedder (Roedder, E., 1972. Composition of fluid inclusions. US Geol. Surv. Prof. Paper 440JJ, p. 164). Although these fluids have the potential of acting as significant metasomatic agents in subduction zones and deep crustal environments, their impact will be mineralogically discernible only if the fluid release and movement is channelized. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Brines; Subduction zone; Deep continental crust

## 1. Introduction

The characteristics of Precambrian crust have often been affected by rock–fluid interaction at all levels (see papers in Bridgwater, 1987). It is thus imperative to understand the characteristics of this interaction, in order to facilitate descrip-

tion of crustal evolution. An important requirement for achieving this goal is quantitative information about fluid composition. The composition and flux of advecting fluids in the crust influence the pressure–temperature conditions at which heterogeneous equilibria occur, and determine the character, magnitude and extent of mass transfer. Mississippi Valley type lead–zinc deposits, uranium roll-front deposits, and fluid mediated transformation of gneisses (Andersen et al.,

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1989, 1990, 1991; Jamtveit et al., 1990) and gabbros (Selverstone et al., 1990, 1992; Philippot and Selverstone, 1991; Thomas, 1991) to eclogites are but a few examples of these processes. In some cases, it has been possible to determine that these fluids are complex, concentrated, high ionic strength brines (e.g. Roedder, 1971, 1972, 1984; Touret, 1985, 1995; Crawford and Hollister, 1986; Philippot and Selverstone, 1991; Selverstone et al., 1992; Pasteris et al., 1995; Samson et al., 1995; Newton et al., 1998). Although phase equilibria have occasionally been used to infer the mole ratios or mole fractions of certain components of these chemical systems, quantitative descriptions of the solution compositions in terms of molalities of principal components has been lacking. What data have been presented are often derived from destructive analyses of fluid inclusions (for example, see Table 5 in Roedder, 1972), but are sparse.

Multiply saturated fluid inclusions provide an important opportunity to expand the available quantitative data set for fluids accompanying the recrystallization processes. Progress in the availability of thermodynamic data for a wide range of solids and aqueous species (see, for example, the compilations in Berman, 1988; Johnson et al., 1992; Johnson and Lundeen, 1994; Berman and Aranovich, 1996; Aranovich and Berman, 1996), and the development of models of activity composition relationships in concentrated aqueous systems (Pitzer, 1973, 1975, 1992; Harvie et al., 1984) have made it possible to compute the standard temperature and pressure (STP; 25°C, 1 bar;) fluid compositions for those cases where fluid inclusions have precipitated multiple solid phases. Although the solubilities for many petrologically important phases are lacking, and the temperature and pressure dependencies of available solubility data are incomplete, the computed STP compositions can provide information regarding the characteristics of the concentrated solutions and their role in metamorphism.

The descriptions of fluid inclusions reported by Selverstone et al. (1990), Philippot and Selverstone (1991) and Thomas (1991) for eclogites from the Monviso ophiolite complex in the Western Alps, provide a good opportunity to conduct such a simulation. Inclusions they interpreted to

be primary were initially trapped at ca. 500°C and 10–11 kbar. These primary fluid inclusions are multiply saturated in a range of salts, and in phases which document the brines were present during the metamorphic development of the eclogites. The work reported here describes the results of numerical simulations to determine the compositions of these brines, and relates these results to other apparent metasomatic eclogite occurrences described from the Western Gneiss Region of the Norwegian Caledonides (Andersen et al., 1989, 1990, 1991; Jamtveit et al., 1990). The results are then compared with observed deep borehole brine chemistries, and a common model is developed describing a mechanism that may be responsible for the formation of brines in these diverse environments.

## 2. Method

In the inclusions inferred to be primary by Philippot and Selverstone (1991) from the Monviso ophiolite complex, various populations of daughter crystals were identified using several analytical techniques. The simulations described here focus on their Type 2 inclusions, which occur as decorations lining oscillatory growth zones within pyroxenes in dilatant eclogite veins and in eclogitic shear fractures. Since the daughter crystals in these inclusions are similar to those in other fluid inclusions they describe, the conclusions reached regarding their Type 2 inclusions are broadly applicable to the suite of inclusion types they recognized, which are reported to occur in garnets, pyroxenes, apatites and albites.

The aqueous speciation code EQ3NR (Wolery, 1992a,b; Wolery and Daveler, 1992) and the reaction path modeling code EQ6 (Wolery and Daveler, 1992; Wolery et al., 1990) were used to compute the equilibrium composition of a fluid saturated in pyrite–hematite–calcite–halite–sylvite–dolomite–gypsum. This assemblage occurs within some Type 2 inclusions, along with rutile, albite, baddeleyite, barite and monazite (Philippot and Selverstone, 1991), which were not included in the simulations because of a lack of data for components of these phases in the HMW

database (see below). The assumed temperature was 25°C (the temperature at which the fluid inclusions are observed to be saturated in these phases). Pressure was assumed to be 1 bar for these initial calculations.

Modeling fluid compositions with these codes requires that an initial speciation calculation be conducted in which the concentrations of dissolved species are computed from specified compositional constraints, such as elemental compositions obtained from chemical analyses, charge balance constraints, or an equilibrium imposed by coexisting solid or aqueous species. The resulting output identifies the concentrations of dissolved species and saturation indices for solids in the specified chemical system. Once a solution composition is obtained, EQ6 is used to compute the equilibrium composition of the aqueous system, taking into account the effects of precipitating the appropriate supersaturated solids. EQ6 can also be used to compute the composition of the aqueous solution–solid system at temperatures along the liquid–vapor saturation curve of water, taking into account dissolution and/or precipitation of the coexisting solids as the intensive variables evolve, provided thermodynamic data are available for the elevated temperatures.

High ionic strength solutions which are saturated in a variety of salts, such as those in this study, can be adequately modeled using the Pitzer (1973, 1975, 1992) description for aqueous species activity–concentration relationships. This model requires specific interaction parameters for ion

pairs in the solution. To date, the available database for these interaction parameters is relatively limited. The compilation by Harvie–Moller–Weare (HMW) database (Harvie et al., 1984) is used in the HMW calculations described below. Because the HMW database does not include data for iron-, silica-, or aluminum-bearing aqueous species or solids, the strategy used here was to compute pH and Eh for coexisting hematite and pyrite, at an initial assumed  $\text{SO}_4^{2-}$  concentration, using the extended Debye–Hückel activity coefficient model of Helgeson (1969), for which data are available for appropriate Fe-bearing species and phases. The resulting Eh and pH approximations were entered in a HMW/Pitzer speciation calculation in which the assemblage calcite–sylvite–dolomite–gypsum–halite was used to constrain total concentrations of Ca, K, Mg,  $\text{SO}_4^{2-}$ , and Na. The  $\text{SO}_4^{2-}$  concentration from this calculation was then used to recompute pH and Eh for the hematite–pyrite system, and the resulting values were used to again compute the chemical properties of the CaO–K<sub>2</sub>O–Na<sub>2</sub>O–MgO–SO<sub>4</sub>–H<sub>2</sub>O–CO<sub>2</sub> system. This iteration process was continued until changes in pH and Eh were less than 0.01 units and 0.3 mV, respectively. Ten iterations were required to achieve this degree of convergence. These pH and Eh values, along with the concentration results from the final FMW/Pitzer simulation were then used in an EQ6 simulation to compute the equilibrium composition of the multiply saturated solution at 25°C. These results are identified in Table 1 under their respective assumed  $\text{HCO}_3^-$  concentrations.

Table 1  
Computed solution compositions (molality) of Type 2 inclusion brines<sup>a</sup>

Solution	$\text{HCO}_3^-$ (2400 mg/l)	$\text{HCO}_3^-$ (100 mg/l)	$\text{HCO}_3^-$ (50 mg/l)	Brine + daughter crystals	Brine + water
Ca	0.013	0.40	0.62	0.77	0.34
Mg	4.16E-03	0.12	0.19	0.23	0.11
K	2.21	1.99	1.90	2.17	1.68
Na	5.25	4.31	3.89	4.56	3.65
Cl	7.04	7.33	7.40	7.75	6.21
$\text{SO}_4^{2-}$	0.211	0.007	0.004	0.096	0.006
$\text{HCO}_3^-$	3.67E-2	6.11E-04	2.82E-04	0.39	5.22E-04
Density (g/cm <sup>3</sup> )	1.48	1.46	1.46	–	1.18
pH	5.38	5.39	5.40	–	5.53

<sup>a</sup> Concentrations are for total dissolved element (for Ca, Mg, Na, K, and Cl), or specific dissolved species (for  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ).

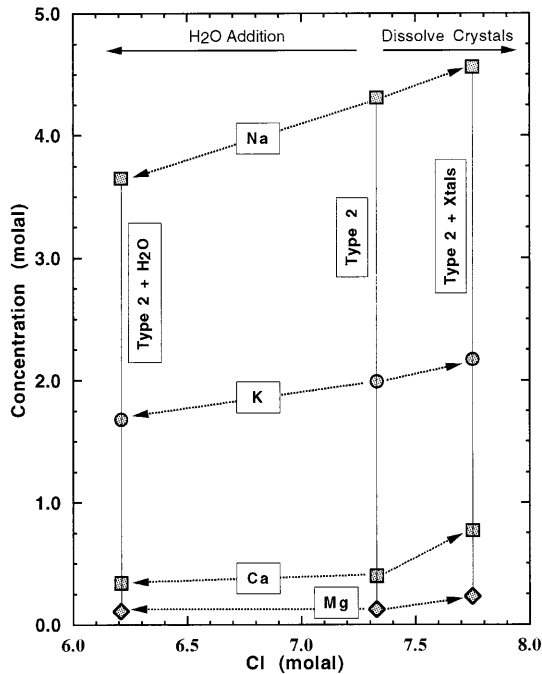


Fig. 1. Computed molalities of Na, K, Ca, and Mg vs. computed Cl molality. 'Type 2' indicates the compositions for the multiply saturated Type 2 fluid inclusions, for the 100 mg/l  $\text{HCO}_3^-$  case (see Table 1 and text). 'Type 2 + H<sub>2</sub>O' indicates the compositions computed for the case in which 20% of the water mass was added to the 'Type 2' inclusion, to account for possible H<sub>2</sub>O diffusion out of the inclusion. 'Type 2 + Xtals' indicates the composition for the case in which sylvite, calcite, halite, gypsum, and dolomite daughter crystals were redissolved into the fluid, as described in the text. Arrowed lines indicate the respective displacements from the nominal 'Type 2' composition for each element.

Since independent constraints could not be placed on  $\text{HCO}_3^-$  concentrations, calculations were conducted for assumed concentrations of 50, 100 and 2400 mg/l. These concentrations were chosen because they reflect the range of  $\text{HCO}_3^-$  concentrations reported for fluid inclusions (generally values greater than 1000 mg/l) as well as deep well brines (generally less than 100 mg/l). The differences in the calculational results are small compared with the range of values reported for brines from fluid inclusions (see Figs. 1–3 and Table 1).

To determine the composition of the solution prior to precipitation of the observed daughter

crystals, small volumes of the daughter crystals were numerically titrated into the in situ brine compositions, in order to 'redissolve' the precipitated daughter crystals. It was assumed that gypsum, dolomite, sylvite, calcite, and halite each accounted for 1.0 vol.% of the inclusion. These volume proportions correspond to molar ratios of 1:1.14:1.99:2.02:2.76, respectively. These results are only illustrative, since neither absolute nor relative volumes of the daughter phases were reported. The results are only shown (Fig. 1 and Table 1 'Type 2 brine + daughter crystals') for dissolving the daughter crystals in the 100 mg/l  $\text{HCO}_3^-$  solutions, since the effect is strictly additive and easily deduced for the other solutions. This calculation will approximately account for the effects of precipitation of these salts during cooling and uplift.

Simulations were also conducted to determine composition limits for the less well constrained Type 1 and 3 inclusions, which lack dolomite and gypsum. The same strategy was followed for these simulations, except that dissolved  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ , respectively, were reduced to an extent sufficient to prevent saturation in dolomite and gypsum. The results are, in general, similar to those for the Type 2 inclusions, and are not discussed further.

An attempt was made to evaluate the brine composition at elevated temperatures, with the precipitated daughter crystals dissolved into the brines. These simulations were conducted at 300°C, and ca. 58 bars (i.e. along the water–steam equilibrium boundary), which is the temperature limit applicable for the 'com' database of the EQ3/6 code package, using the extended Debye–Hückel activity coefficient model. This database and activity coefficient model were used because the data for the HMW/Pitzer activity coefficient model do not extend to elevated temperatures. However, the results obtained were generally incompatible with those obtained using the HMW/Pitzer activity coefficient model at low temperature, due to the fact that the extended Debye–Hückel activity coefficient model is highly inaccurate at the high ionic strengths encountered in these solutions. As a result, these high temperature calculations are not considered further here.

### 3. Results

The computed solution compositions for the Type 2 inclusions are high ionic strength (7.8–8.2

mol), slightly acidic (pH approximately 5.4) brines with water activities of approximately 0.7 (Table 1). Total dissolved solids account for approximately 20–40% of the mass of the solutions.

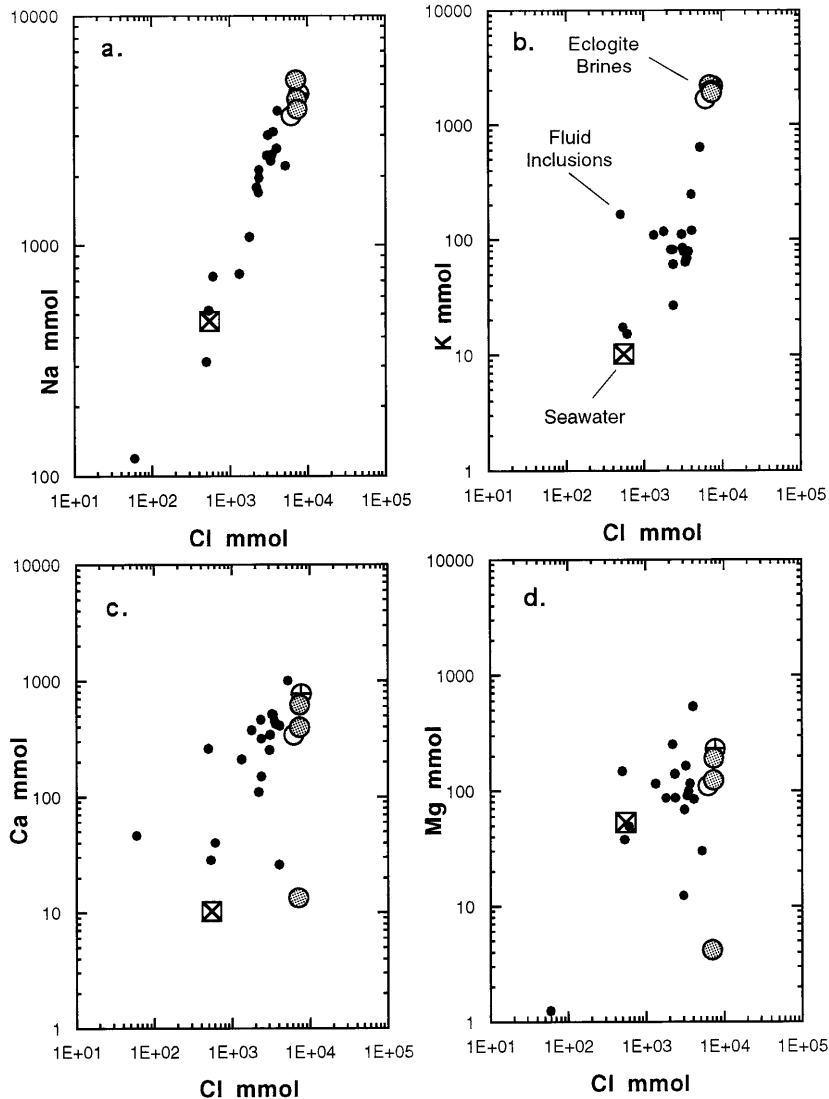


Fig. 2. Comparison of computed concentrations of eclogite fluid inclusions ('eclogite brines') with seawater ('seawater', crossed box) and destructively analyzed fluid inclusions ('fluid inclusions', small filled circles; Roedder, 1972). (a) Na, (b) K, (c) Ca and (d) Mg vs. Cl. The 'eclogite brines' symbols are, shaded circles — analyses in Table 1 for the three different  $\text{HCO}_3^-$  concentrations; crossed open circle — brine with daughter crystals added to the 100 mg/l  $\text{HCO}_3^-$  brine in Table 1; open circle — brine with 20% water added to the 100 mg/l  $\text{HCO}_3^-$  brine in Table 1. The computed compositions for Cl, Na and K represent the most concentrated solutions within this data set. Even so, the computed eclogite fluid inclusion compositions fall along compositional variation trends suggested by the analyzed fluid inclusion data set.

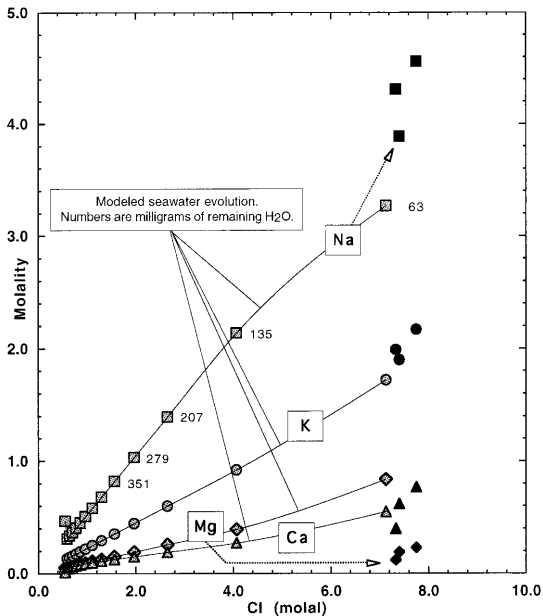


Fig. 3. Computed molality of Na (squares), K (circles), Ca (triangles), and Mg (diamonds), vs. Cl, for the eclogite fluid inclusion compositions (solid symbols), and for the modeled seawater–basalt system (connected shaded symbols). The numbers by the shaded symbols along the Na trend are the number of milligrams of water remaining from 1 kg of water, during the H<sub>2</sub>O removal stage of the simulated seawater–basalt evolution. Only the last five steps in the reaction progress are enumerated. The initial fluid composition used in the H<sub>2</sub>O removal process is that resulting from interaction of 0.04 mol of anorthite and 0.12 mol of potassium feldspar with seawater.

Computed 1 bar solution densities are approximately 1.2–1.4 g/cm<sup>3</sup>.

The primary source of uncertainty in the compositions comes from the lack of information for the concentration of HCO<sub>3</sub><sup>-</sup> (see Table 1 for comparison of results). Because the bicarbonate concentration determines carbonate speciation and the saturation index for solid carbonates, total Ca and Mg are most strongly influenced by the assumed initial bicarbonate concentration. The results indicate an inverse, linear correlation between HCO<sub>3</sub><sup>-</sup>, and Ca and Mg · Na, K and Cl are only slightly influenced by this effect, and their respective concentrations are thus much better constrained.

Regardless of the effects of initial assumed HCO<sub>3</sub><sup>-</sup> concentration, these are predominately Na- and K-rich brines, with subordinate Ca and Mg. The approximate Na:K molar ratio is 2.1–2.5, over the range of HCO<sub>3</sub><sup>-</sup> concentrations, while the Na:Ca:Mg ratio varies between 1:0.2:0.05–1:0.003:0.0001. Charge balance is primarily maintained by the very high Cl concentrations.

The elemental ratios and aqueous species activities of these brines do not bear any systematic relationship to those in seawater. Enrichments of elements, and the respective activities of the dominant aqueous species, relative to seawater, are K (100 ×, 300 ×), Cl (10 ×, 10 ×), and Na (6 ×, 30 ×). The relative concentrations and activities for Ca are either at or above that of seawater, and for Mg are greater than or less than that of seawater, depending upon HCO<sub>3</sub><sup>-</sup> concentration, which is unknown. Sulfate maintains a dramatic depletion, relative to seawater, at low HCO<sub>3</sub><sup>-</sup> values, but is enriched at high HCO<sub>3</sub><sup>-</sup>.

## 4. Discussion

### 4.1. Bounding the real brine compositions

Philipot and Selverstone (1991) noted the possibility that these inclusions may have experienced necking or decrepitation at some point during their ascent. Such effects would make it impossible to determine the exact composition of fluid present during metamorphism. However, certain characteristics about the solutions allow conclusions to be reached regarding the primary chemical features of the solutions present during recrystallization. The observation that briny inclusions consistently occur as decorations along growth zoning in the clinopyroxenes, and that these particular eclogites developed by fluid-mitigated mass transport, requires the presence of saline fluid during eclogite formation. The occurrence of calcite-, sylvite-, and halite-saturated fluid inclusions in garnets, pyroxenes, and apatites also argues that re-equilibration of the inclusion solutions may not have been extensive, given the contrasting mechanical and physical properties of these mineral phases.

Experimental investigations have shown that salinities can be enhanced as much as 20–30 wt.% in salt-rich inclusions trapped at elevated temperatures and pressures (1.5–3 kbar, 600–850°C), when they cycle down to lower pressure conditions (Hall and Sterner, 1993). Diffusion of H<sub>2</sub>O out of the inclusion and into the enclosing silicate framework is the proposed mechanism through which salinity increases are effected. The composition of the inclusions with water added back into the fluid (Table 1, 'Type 2 brine + water') was determined by numerically titrating H<sub>2</sub>O into the brine that is computed to be in equilibrium with the daughter crystals. Although this results in lower salinities, the brines are still an order of magnitude more concentrated than sea water, and maintain compositional characteristics (e.g. molar ratios) different from sea water.

The occurrence of calcite-, sylvite-, and halite-bearing fluid inclusions in garnets, pyroxenes, and apatites requires that the parent brines were in equilibrium (i.e. saturated) with these silicate and phosphate phases at the conditions of fluid entrapment. Hence, these solutions must contain significant concentrations of Si, Al, P, and Fe, in addition to all of the other components modeled here, and those noted by Philippot and Selverstone (1991). Selverstone et al. (1992) noted this fact as well. However, currently there are no appropriate thermodynamic data available to determine the concentrations of these elements in the brines.

These points suggest that the computed fluid compositions for these brines are an approximation to the actual compositions of the solutions at the time of entrapment. Preferential water loss, precipitation of daughter minerals, possible decrepitation/necking, and the presence of a number of components in solution that cannot be quantitatively modeled, are the primary causes of uncertainty. Regardless of these effects, the overall compositional characteristics of these brines would not be profoundly changed if these effects could be resolved. It remains evident that the solutions responsible for development of these eclogites were concentrated Na- and K-rich brines that also possessed high concentrations of Ca and Mg, with very high chloride and sulfate contents.

Comparison of these computed compositions with destructive analyses of fluid inclusions from metamorphic rocks (Roedder, 1972) indicate that the eclogite fluid inclusions consistently fall within the trends defined by the analyzed samples, for Na, K, Ca, and Mg versus Cl (Fig. 2). However, in all cases, the eclogite inclusions have compositions that are at the high Cl, Na, and K ends of these trends.

These observations suggest that the composition of the fluids present during entrapment were similar to those reported from other saline fluid inclusions, although the primary cations (Na and K) and anion (Cl) may have been more concentrated than in any other reported analysis.

#### 4.2. Fluid densities

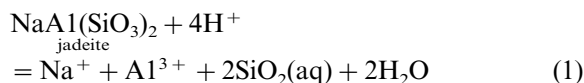
The computed densities of these brines (Table 1) are much higher than those assumed by Philippot and Selverstone (1991). The difference in densities reflects the fact that they determined the inclusion density by comparing melting temperatures with measured values in known binary and ternary systems. As they noted, the presence of other components (e.g. Ca, S, Fe, Mg, etc.) will have an unknown effect on computed densities derived from such systems. Although isochores cannot be accurately constructed for these complex fluids in the absence of appropriate PVT data, it is likely that the trends of isochores for these brine compositions will more closely approach the assumed eclogite conditions of formation ( $450 \leq T \leq 550^\circ\text{C}$ ;  $10 \leq P \leq 11$  kbar) than those previously constructed by Philippot and Selverstone (1991).

#### 4.3. The role of concentrated aqueous solutions in high pressure environments

Previous studies have concluded that eclogites from deep crustal and subduction environments may form in the presence of water-rich fluids (e.g. Holland, 1979). That conclusion is consistent with the results presented here, in the sense that these are aqueous solutions in which H<sub>2</sub>O/CO<sub>2</sub> ratios are very high (> 0.9). However, the actual water mole fractions are computed to be approximately

0.8, with a resulting water activity computed to be approximately 0.7, at STP. The actual activity of water in these brines at the  $T$  and  $P$  of entrapment is somewhat problematic, in that activity–composition relationships for  $H_2O$  in concentrated brines at high pressures is still under investigation (Aranovich and Newton, 1996). From the data of Aranovich and Newton (1996), the water activity under the conditions of entrapment would be approximately 0.6.

Lowering the water activity by such a degree will result in significant modification of the  $PT$  equilibrium conditions for dehydration reactions. However, although water activity is an important equilibrium parameter in phase relationships in subduction zones, it alone cannot control the phase equilibria in the system, since the chemical potentials of the dissolved constituents in solution must also influence phase stability. Although the magnitude of these compositional effects cannot be quantified since neither adequate models nor data for the thermodynamic properties of the dissolved species in concentrated brines at high temperatures and pressures are available, it may be argued that high activities of dissolved species may have effects that counterbalance those of low water activities for some equilibria. For example, the equilibrium condition for the hydrolysis reaction for jadeite



is a direct function of both the water activity and the activities of the dissolved species in solution. In concentrated brines similar to those in the Type 2 inclusions, the  $\text{Na}^+$  ion activity, at STP, is ca. 9.6, which is an order of magnitude greater than the activity of water in the inclusions at these conditions. This contrast in activity is more than sufficient to counterbalance the phase equilibrium shift associated with the lower water activity, and would thus stabilize jadeite at lower pressures.

Recent work (e.g. Frantz et al., 1992; Joyce and Holloway, 1993; Duan et al., 1995) has demonstrated that brine-rich systems at elevated temperatures and pressures will consist of two immiscible solutions, one of which is predominately  $\text{NaCl}$ –

$\text{H}_2\text{O}$ , and the other predominately  $\text{CO}_2$ – $\text{H}_2\text{O}$ . The compositional effects on phase stability described above are complicated by the potential separation of these immiscible solutions. Although the chemical potentials of the dissolved constituents must be equal in the different solutions, if they are in equilibrium, migration of one solution at rates or along pathways that are different from the other solution will result in reequilibration and exchange of dissolved components with solids and liquids along the migration pathways, leading to different chemical evolutions for the separated solutions. The highly complex phase relationships on local scales, described by Selverstone et al. (1992) and attributed to fluid variability and immiscibility, are good examples of what would be expected as such phase separation and fluid migration occurs. On regional scales, complex juxtapositioning of metamorphic facies may be expected, as well as changes in trace and bulk element compositions. On this basis, brines such as these must be considered potentially profound metasomatizing agents.

Movement of these brines from a subducted slab into an overlying mantle wedge, accretionary prism, or overriding continental mass would result in some form of ‘alkali metasomatism’. However, the nature and extent of the alteration depends upon the specific ion considered, and the release scenario. In the following discussion, it is assumed that the fluid volume fraction is between  $10^{-3}$  and  $10^{-5}$ , that the Cl and K molalities in the solution are 7.4 and 1.9, respectively, and subduction rates are ca. 10 cm per year. For these fluid volume fractions, Cl mass is between  $3.7\text{e}8$  and  $3.7\text{e}6$   $\text{kg}/\text{km}^3$  of subducted crust, and the respective K mass is between  $1.0\text{e}8$  and  $1.0\text{e}6$   $\text{kg}/\text{km}^3$  of subducted crust. Because these masses are relatively small, the likelihood of developing observable chemical or mineralogical alteration associated with brine migration is small, unless fluid flow is concentrated along preferential flow paths. This is precisely the condition that is reported to be responsible for the development of eclogite in both the Monviso ophiolite complex and the Western Gneiss Region of Norway. For the Monviso complex, where eclogite formation was concentrated in flow regimes on the scale of tens of meters, the assumptions above would re-



sult in Cl and K fluxes in the order of tens of kg/m<sup>2</sup> per year. In the case of the Western Gneiss Region of the Norwegian Caledonides, transformation involved water-rich fluids that were saturated in calcite and nahcolite at the time of eclogite formation. The reactions responsible for this transformation require transfer of significant masses of Na, K, Ca, Al, Mg, and Si into and out of the system along well defined flow paths (Jamtveit et al., 1990). Although there is insufficient information to determine much about the composition of these solutions, saturation in calcite and nahcolite suggests that the Na concentration exceeded 3.0 mol, and that total carbonate aqueous species exceeded that in the Monviso eclogites, in order to stabilize the nahcolite–calcite assemblage.

#### 4.4. *Origin of the brines*

The elevated Cl/H<sub>2</sub>O molar ratio in these brines suggests an origin from seawater. Brines have been observed in fluid inclusions from fracture zones in the mid-Atlantic Ridge (Roedder and Coombs, 1967; Stakes and Vanko, 1986; Kelley and Delaney, 1987; Vanko, 1988; Vanko et al., 1992), and from subduction sequences (Cowan and Cann, 1988; Kelley and Robinson, 1990; Scambelluri et al., 1997), demonstrating that the formation of concentrated brine from seawater is an integral part of alteration of oceanic crust and mantle, prior to and during subduction. Mechanisms responsible for brine development that have been proposed include seawater–rock interaction (e.g. Seyfried and Ding, 1995; Seyfried et al., 1991; Travis et al., 1991; Goldstein et al., 1992) with and without phase separation (Berndt and Seyfried, 1993, 1997; Berndt et al., 1988, 1989).

Assuming that brine forms during alteration and metamorphism of the oceanic crust, a model was constructed to see if the fluid inclusion compositions modeled for the eclogites, could be reproduced. In this model, rock–seawater interaction dissolves the far-from-equilibrium primary igneous mineral phases, and precipitates secondary mineral suites. This process consumes H<sub>2</sub>O, as hydration reactions occur. To reproduce this process, a model system was constructed in

which seawater was reacted with one or more mineral phases along a reaction progress path, and the resulting solution was then enriched by progressive removal of H<sub>2</sub>O. Simulations using this scenario were conducted at 25°C, at specified CO<sub>2</sub> fugacities. The simplified closed-system rock–water interaction simulations were conducted using the composite database (version R22a) of EQ3/6, since it contains an adequate database for a wide range of silicate phases. Because high ionic strength solutions would develop as water is progressively removed, the Pitzer activity composition relationships, and related HMW database, were used to model the H<sub>2</sub>O-removal process. Since there are limited data for ion interaction parameters, only Ca, Na, K, Mg, sulfate, and bicarbonate were considered during the water removal stage of the modeling. No redox effects were considered, nor were oxygen fugacities constrained, due to the absence of redox couples in this database. These constraints limited the simulations to the feldspar (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>–NaAlSi<sub>3</sub>O<sub>8</sub>–KAlSi<sub>3</sub>O<sub>8</sub>) component of basaltic compositions.

A broad range of feldspar end member ratios were attempted, with the target composition at the end of the reaction process being that of the computed eclogite fluid inclusion chemistry. The results, which provided the best fit (Fig. 3) consumed 0.04 mol of anorthite and 0.12 mol of potassium feldspar dissolved in seawater, with 93.7% of the H<sub>2</sub>O removed. The initial product minerals of the seawater–silicate interaction are K-rich nontronite clay, quartz, alunite (a potassium sulfate), and dawsonite (an hydrated sodium–aluminum carbonate). This assemblage (clay–carbonate–quartz) mimics an initial basalt hydration mineral assemblage. As removal of water proceeds, chlorites also form. Upon removal of > 90% of the H<sub>2</sub>O, the final mineral assemblage is anhydrite–dolomite–halite–sylvite, which is similar to the daughter crystal mineral assemblage observed in the fluid inclusions. Because the water removal portion of the simulation was conducted using the HMW database, neither sulfide–sulfate nor other redox-sensitive equilibria could be considered, nor silicate–water interaction or silicate formation. Despite these limitations, this scenario is analogous to equilibrating

seawater with the felsic (anorthite) and glass (alkali feldspar) components of basalt, while allowing hydration of Mg- and Fe-bearing silicates and glass (mimiced by H<sub>2</sub>O removal) during subduction. The end result produces fluids remarkably similar in composition and saturation conditions to those seen in the Type 2 inclusions, with the exception of Mg, which is overestimated in the solutions, relative to the composition deduced for the inclusions. This short-coming reflects the inability to incorporate Fe–Mg-silicates in the H<sub>2</sub>O removal stage of the simulations, where serpentine formation would play an important role in the Mg mass balance. It is noteworthy that this degree of similitude could be achieved at such low temperatures, suggesting that the briny nature of the solutions accompanying subduction zone processes, even to depths of tens of kilometers, may be inherited from seafloor alteration or in the shallowest levels of subduction zones.

## 5. Conclusions

The composition of the aqueous phase in multiply saturated fluid inclusions can be computed using aqueous speciation/reaction path codes such as EQ3/6. For fluid inclusions described from eclogites recovered from the Monviso ophiolite (Selverstone et al., 1990; Philippot and Selverstone, 1991; Thomas, 1991), the resulting compositions are those of high density, high ionic strength brines in which total dissolved solids account for ca. 20–40% of the mass of the solutions. The brines are K-, Na-, and Ca-rich, and have relatively low water activities (ca. 6–7, at STP). The densities of the solutions are computed to be ca. 1.2–1.4 g/cm<sup>3</sup>, and may have isochores that more closely approach the actual entrapment conditions than previously expected.

The properties of these fluids are such that phase equilibria involving H<sub>2</sub>O may experience significant shifts in equilibrium *P–T* conditions, even at relatively water-rich, CO<sub>2</sub>-poor conditions. However, the high activities of the dissolved species in these brines may offset these effects. This suggests that current models of phase relationships in subduction zone complexes require

further embellishment, in order to account for the influence of both the high concentration of dissolved species and the lower water activities in these brines.

Slab-derived mass transporting fluids have played a role in numerous models of subduction zone processes (e.g. Gill, 1981; Peacock, 1990; Selverstone et al., 1992; Brennan et al., 1995). The results reported here place constraints on the magnitude of that role. The high activities of the dissolved species in the Monviso eclogitic brines imply that these brines may be profound metasomatizing agents, resulting in significant recrystallization and transfer of mass, but only if fluid flow pathways are channelized. If fluid movement is broadly distributed through the crust or mantle, very little secondary phase development would occur.

The complex compositions of these brines suggests that they could play a role in a wide range of apparently contradictory metamorphic transformations. For example, brines appear to play a role in the development of granulite facies gneisses (Touret, 1985, 1995; Aranovich et al., 1987; Newton et al., 1998), but they may also be responsible for the observed transformation of granulites to eclogites and amphibolites (Andersen et al., 1989, 1990, 1991; Jamtveit et al., 1990). These differences are likely to reflect regional differences in the activities of key components in the solutions, including H<sub>2</sub>O, Na, Si, Ca, Mg and K.

Although the fluid composition can be approximately reproduced by using a relatively simple model of seawater–basalt interaction, with associated loss of water through hydration reactions, the assumptions required to make the calculations are broad. Further work needs to be done to develop well constrained, quantitative estimates of the extent of fluid–rock interaction.

Regardless of the fluid volumes, the presence of highly concentrated brines at spreading centers, in ophiolites, within subduction zones, and within deep crustal environments implies that brines are intimately associated with oceanic and continental crust during many phases of their evolution. The effect of these ca. 5–8 mol solutions on phase relationships and processes within crustal regimes deserves further attention.

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