Lead and bromine enrichment in eclogite-facies fluids: Extreme fractionation during lower-crustal hydration

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ABSTRACT

Hydration reactions associated with eclogite-facies metamorphism of granulites in the Norwegian Caledonides led to the formation of saline brines with exceptional compositions. Primary omphacite- and garnet-hosted fluid inclusions from Norwegian eclogites formed by hydration of granulites contain a plethora of solid phases. A total of 18 different minerals have been identified in multiphase brines, and 12 of these occur at the Bådsholmen locality in Sunnfjord. Fluid inclusions from this locality are characterized by a high Br/Cl mass ratio (0.03) and extreme Pb enrichment as demonstrated by the presence of Pb-bearing daughter minerals including galena, a Pb-Cl–bearing phase, and a Pb-Cl-Br–bearing phase. The fluid compositions may reflect enrichment of elements incompatible with the silicate structure during consumption of H_2O by eclogite-forming hydration reactions. Pb is believed to have been scavenged from the parent granulite by the increasingly saline brine during K-feldspar breakdown.

INTRODUCTION

Primary brine fluid inclusions in omphacite are documented from a number of eclogites (i.e., Philippot and Selverstone, 1991; Selverstone et al., 1992; Andersen et al., 1993; Nadeau et al., 1993; Giaramita and Sorensen, 1994; Vallis and Scambelluri, 1996; Scambelluri et al., 1998) and represent evidence for the presence of a free fluid phase during deep-crustal metamorphism. Hydration reactions are common during eclogite formation, and during deep-crustal metamorphism in general, in cases where the precursor is anhydrous (e.g., granulites). The infiltrating fluid may significantly change its chemistry during the hydration process, as is evident from increasing inclusion-fluid salinities (e.g., Scambelluri et al., 1998) and gradually increasing incorporation of Cl into silicate structures (e.g., Kullerud, 1996). The extreme end of this process is represented by a total consumption of the fluid phase and precipitation of solid salts in the available pore space (Markl and Bucher, 1998).

Continental rocks of the Western Gneiss region of south Norway (Fig. 1) underwent high-pressure metamorphism during the Caledonian orogeny that at least locally reached the stability fields of coesite (e.g., Wain, 1997). Eclogite-facies rocks occur throughout the Western Gneiss autochthon and within allochthonous units of the Bergen arc system. The eclogite-facies rocks are generally regarded as a result of prograde metamorphism of amphibolite-facies protoliths (e.g., Krogh, 1982; Jamtveit, 1987) or as a result of direct, water-mediated metamorphism of Precambrian granulites or igneous rocks (e.g., Austrheim and Griffin, 1985; Jamtveit et al., 1990). Fluid-inclusion studies document the presence of both H_2O-N_2-CO_2 fluids and brines in eclogite minerals (e.g., Andersen et al., 1989, 1993). Multiphase brine inclusions in omphacite from the Western Gneiss region, previously reported briefly by Andersen et al. (1993), are described in detail in this paper.

The eclogites studied in this work are from three localities in the Western Gneiss region (Bårdsholmen, Engebøfjellet, Leknes) and one locality in the Bergen arcs (Holsnøy) that underwent regional low- to medium-temperature eclogite-facies metamorphism (~500–650 °C). The localities are situated within a 140-km-long section of west Norway (see Fig. 1). These eclogites are all mafic, i.e., they contain relatively small amounts of mica, kyanite, and quartz, and are found as lenses or pods (up to several hundred meters in size) surrounded by various types of gneisses. Field, petrographic, and geochemical evidence suggests gabbroic or granulitic precursors to these eclogites. The omphacites and garnets in these eclogites contain fluid inclusions, in contrast to nearby, more felsic eclogites that are rich in kyanite, mica, and quartz but that lack fluid inclusions.

Bårdsholmen

At Bårdsholmen (Fig. 1), layered Proterozoic granulites (mafic and leucocratic layers) and Caledonian eclogites are closely associated. Eclogites occur (1) as lenses in felsic eclogite-facies gneisses or amphibolite-facies gneisses and (2) as layers (originally composed of mafic granulite) in the
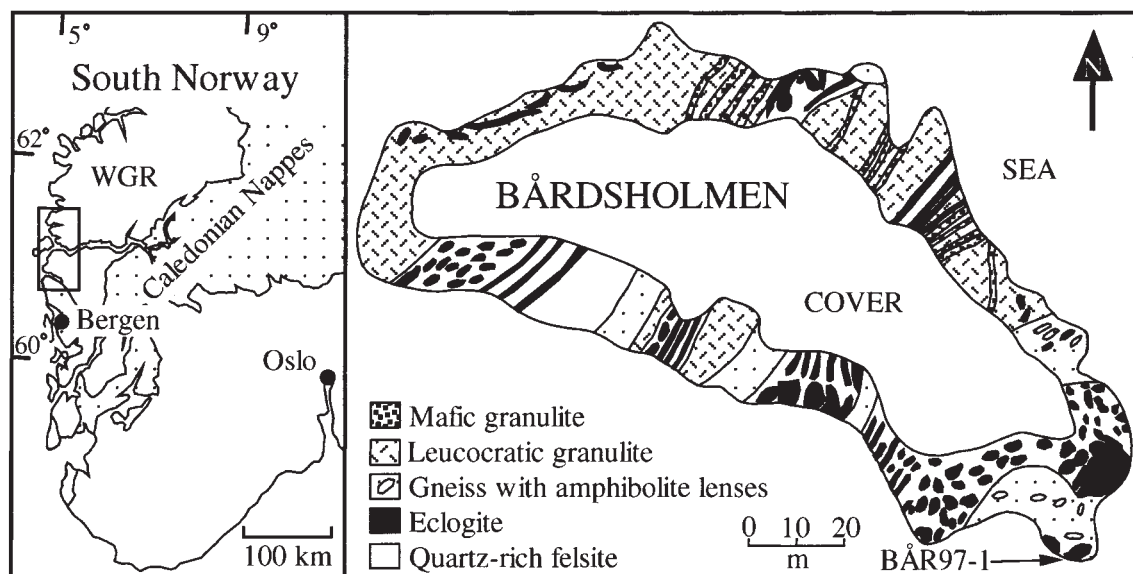

Figure 1. Geology of Bårdsholmen and map of southern Norway showing area of sampling (rectangle). WGR is Western Gneiss region.

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leucocratic granulite. The field distribution suggests formation of eclogites along fractures in the mafic granulite, and the degree of eclogitization varies accordingly. Eclogite-facies mineral assemblages are found along these fractures where they cut the leucocratic granulite. The amphibolite-hosted eclogites contain up to 46% (by volume) omphacite, 35% garnet, and 18% hydrosilicates, whereas the felsic eclogite-facies gneisses are composed of quartz (~75%), mica (~20%), and epidote (~5%). Amphiboles present in the felsic eclogite-facies gneisses and the partly eclogitized leucocratic granulites contain up to 3.8 wt% and 6 wt% Cl, respectively. Austrheim and Engvik (1997) have suggested that the eclogites at Bårdsholmen formed as a result of limited fluid infiltration into the granulites during deformation.

OMPHACITE-HOSTED FLUID INCLUSIONS

Fluid inclusions are abundant in omphacites of the mafic eclogites from west Norway. They are elongated parallel to the *c*-axis and range in size up to ~110 µm in length. A primary or pseudosecondary origin is indicated by (1) occurrence in three-dimensional arrays (Fig. 2) and, in some cases, (2) fluid inclusions that apparently nucleated on omphacite-hosted rutile crystals. Furthermore, they are not accompanied by breakdown of omphacite to amphibole.

All fluid inclusions contain liquid water and a vapor bubble along with several solid phases (Fig. 3A). The solid content of fluid inclusions in the omphacites varies considerably both within one sample and between different localities.

Optical microscopy, scanning electron microscopy (SEM; at the University of Oslo and the University of Leeds), and Raman spectroscopy (a multichannel Dilor XY Raman spectrometer at the University of Stockholm) have been used to identify solid phases within the fluid inclusions. For the SEM analyses, centimeter-sized, freshly broken pieces of eclogite were mounted on glass slides and carbon coated; the opened fluid inclusions were easily found on omphacite cleavage surfaces.

All fluid inclusions contain solid phases, commonly including calcite, gypsum, and metal-bearing sulfides (Table 1). The degree of fill by solids is generally in the range of 20–50 vol%. There is an important difference between solids precipitated within a fluid inclusion from the inclusion fluid (daughter crystals) and those formed within the inclusion as a result of interaction between inclusion fluid and host mineral. The latter are here termed *step-daughter* crystals, since they contain components from both fluid and host. Fluid inclusions within each sample are all similar in appearance and contain a similar suite of daughter and step-daughter crystals. Calcite crystals are ubiquitous (see Table 1) and could be daughter or step-daughter crystals (cf., Andersen et al., 1984; Heinrich and Gottschalk, 1995). Quartz, feldspars, and iron-bearing sulfides also occur within fluid inclusions and may partly be products of retrograde mineral and fluid interactions. Microthermometry and
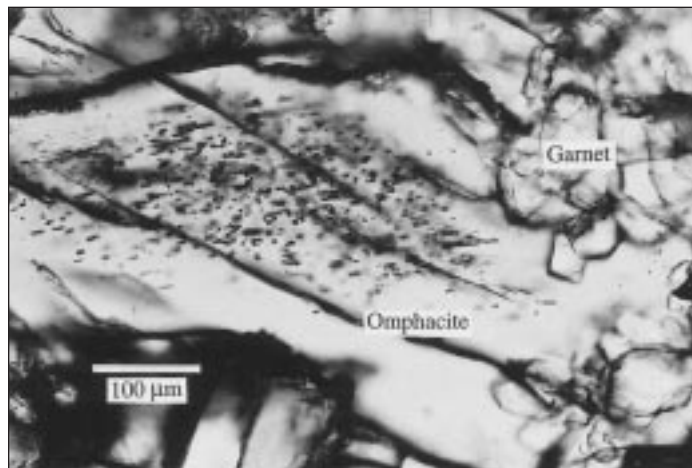
Raman spectroscopy gave no indication of the presence of CO_2, suggesting that CO_2 availability controlled the extent of the calcite-forming reaction. In addition, multiphase brine inclusions in garnets contain up to seven solid phases including calcite, chalcopyrite, amphibole, and several unidentified silicates. Differences between suites of step-daughter crystals in omphacite and garnets are to be expected because of differences in host chemistry. Garnet-hosted fluid inclusions will not be discussed in detail in this paper.

Fluid Inclusions in Eclogite from Bårdsholmen

At Bårdsholmen, fluid inclusions occur in omphacites from an eclogite lens ~4 m long (Fig. 1). Three samples from this eclogite contain omphacites with ubiquitous, primary, halite-bearing fluid inclusions (Fig. 2) that contain similar suites of daughter and step-daughter crystals (Table 2). The fluid inclusions range in size up to ~25 × 8 µm. Generally, the omphacite rims are free of fluid inclusions.

Halite and calcite have been identified with the SEM (calcite was confirmed by its Raman spectrum) and are easily seen under the optical microscope in most fluid inclusions from this eclogite. The Zn-S phase is likely sphalerite, and the Fe-Ni-S phase is probably pentlandite. The Zn-S phase is possibly a daughter crystal, and the Fe in the Cu-Fe-S phase (possibly chalcopyrite) could be derived from omphacite. Irregularly shaped, mixed chloride phases (Na-Ca-K-Cl) identified in some opened fluid inclusions are probably precipitates formed during opening. Quartz and K-feldspar could have formed during retrograde fluid and mineral reactions.
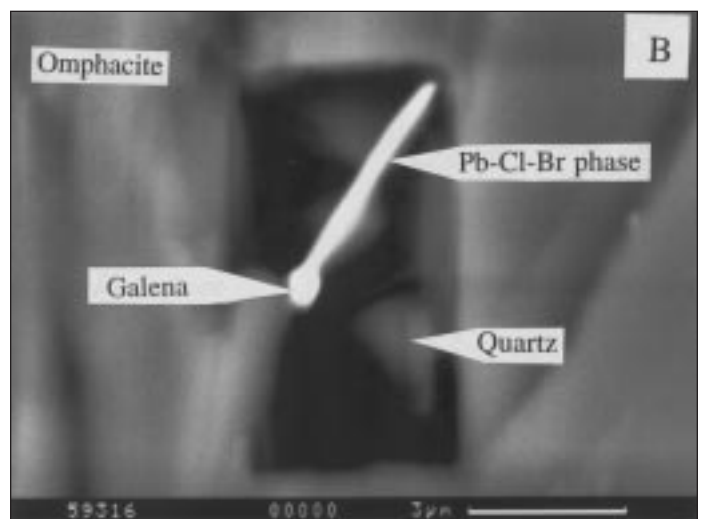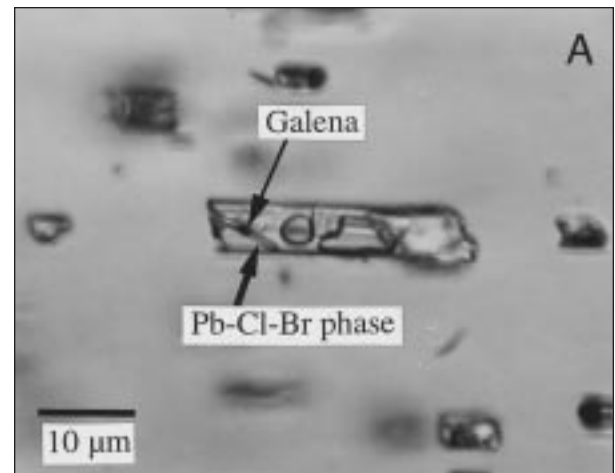
Figure 3. A: Multiphase fluid inclusion in omphacite from sample BÅR97-1; inclusion contains several solid phases, brine, and a gas bubble. B: SEM backscatter photomicrograph of opened fluid inclusion from sample BÅR97-1, showing two Pb-bearing phases.

Figure 2. Photomicrograph of fluid-inclusion–bearing omphacite crystal from sample BÅR97-1. Note virtual absence of fluid inclusions near omphacite margins.

TABLE 1. SOLID PHASES IN OMPHACITE-HOSTED FLUID INCLUSIONS

Sample	Phases
BÅR97-1	calcite, quartz, K-feldspar, rutile, NaCl, Na-Ca-K-Cl Cu-Fe-S, Zn-S, Fe-S-Ni, Pb-Cl*, Pb-S, Pb-Cl-Br
EN97-5	calcite, quartz, K-feldspar, albite, gypsum, rutile Na-Cl*, Fe-Cu-As-S
EN97-8	calcite, quartz, gypsum, Na-Cl*
LE1	calcite, quartz, albite, gypsum, amphibole, Na-Cl* Fe-Cu-S
HA12/93	calcite, Na-Cl*, Fe-Cu-S, Fe-oxide

Note: All phases were identified using SEM. Calcite, quartz and gypsum were identified with Raman as well.
*possibly precipitated during opening of the inclusions.

TABLE 2. FLUID-INCLUSION HALOGEN CONTENT

Sample	NaCl wt%	Cl ppm	Cl/Br	Br ppm
BÅR97-1	50	303 300	33	9191
EN97-5	20.9 (2.9)	126 779	106	1196 (166)
LE1	23.0 (1.0)	145 584	124	1174 (49)
HA12/93	22.9 (1.5)	138 911	244	569 (37)
EN97-8	22.0 (2.0)	133 452	395	338 (31)

Note: standard deviations are given in parentheses.

Three Pb phases were identified from opened fluid inclusions by SEM: Pb-S, Pb-Cl-Br (Fig. 3B), and Pb-Cl. The Pb-S and Pb-Cl-Br phases usually occur together in the same fluid inclusion, and they are visible under the optical microscope. The Pb-Cl phase is only observed in the SEM and coexists with other Pb phases; it may be that it precipitated during opening of the inclusions. The small size of the Pb-bearing phases makes quantitative analysis difficult, but the Pb-S phase is likely galena, and the Pb-Cl phase is probably $PbCl_2$, though it could possibly be a Pb-Cl hydroxide. A Pb-Cl-Br phase has not previously been reported from nature to our knowledge. It is possible that this phase is a $PbCl_2$-$PbBr_2$ solid solution. We infer that the galena and the Pb-Cl-Br phase are daughter crystals, formed within the inclusions prior to opening, on the basis of the well-developed crystal shape and similarities between textures seen in fluid inclusions under the optical microscope and those seen with the SEM (cf. Fig. 3A and 3B). Galena also occurs in opened fluid inclusions in garnet from Bårdsholmen.

RECONSTRUCTING CHEMISTRY OF THE INCLUSION FLUIDS

Methods used for reconstructing the fluid composition at Bårdsholmen include microthermometry, crush-leach analyses, and back-calculations based on volume estimates of daughter crystals.

Microthermometry

Final-ice-melting temperatures of the inclusion brines were measured on Linkam heating-freezing stages at the University of Leeds and the University of Oslo. First-melting temperatures were not systematically measured, but are generally as much as 8 °C lower than the eutectic in the H_2O-NaCl system. Heating of the inclusions resulted in homogenization of the vapor phase to liquid generally in the range of 300–420 °C; decrepitation occurred at temperatures above 450 °C. Apparent salinities in the H_2O-NaCl system were calculated by using freezing-point depression relationships given by Bodnar (1993); the calculations yielded salinities in the range of 18–24.5 wt% NaCl equivalent. Dissolution of halite in one sample (BÅR97-1) occurred between 470 and 555 °C (10 measurements with a mean of 511 °C). The minimum apparent salinity for the halite-bearing inclusions (halite-dissolution temperatures from Chou, 1987) was estimated from the maximum vapor-liquid homogenization temperature (i.e., 420 °C), since vapor-liquid homogenization occurred before halite dissolution, giving 50 wt% NaCl equivalent (Table 2).

Crush-Leach Analyses

Bulk populations of fluid inclusions from the described localities have been analyzed for Cl and Br by using the crush-leach method (Bottrell et al., 1988; Banks and Yardley, 1992). Omphacites were handpicked from a 500–1000 μm size fraction of crushed eclogite, and ~1–2 g of omphacite (purity: 95%–100%) was cleaned with boiling water prior to crushing and leaching. The leachate was analyzed with a DIONEX 4500i liquid-ion chromatograph. The resulting Cl/Br mass ratios are given in Table 2. To calculate apparent Br concentrations in a population of inclusion fluids, Br/Cl

ratios were multiplied with the population's average Cl content obtained by freezing and heating measurements. All the analyzed Norwegian eclogite brines show a trend toward Br enrichment and decreasing Cl/Br ratios (Fig. 4); the Pb-rich Bårdsholmen sample falls at the Br-rich end of this trend (minimum Br content of 9191 ppm).

Estimates of Pb Concentrations

The volumes of Pb daughter crystals were measured from SEM backscatter photomicrographs of opened fluid inclusions and then were used to recalculate the concentrations of Pb in the original fluid. The calculations assumed that (1) the daughter crystals are $PbCl_2$ and PbS, (2) the shape of the fluid inclusions is prismatic, and (3) the fluid density is 1.2 g/cm^3 (roughly the density of a high-salinity brine at eclogite-facies conditions). Calculations from 19 inclusions, ignoring Pb in solution, gave an average of 81 300 ppm, and a standard deviation of 60 100 ppm. Even though the errors are considerable, the lower limits still exceed all Pb analyses of natural waters and inclusion fluids. The volume of calcite in the inclusions has been used to calculate the mole percent of CO_2 in the original fluid, giving values ranging from 2% to 12%.

DISCUSSION

In natural solutions, Pb is usually complexed by Cl, and concentrations of up to several hundred parts per million have been reported from basinal brines (e.g., Carpenter et al., 1974; Sverjensky, 1984). Magmatic brines may contain up to several thousands of parts per million Pb (e.g., Heinrich et al., 1992; Campbell et al., 1995).

There are two end-member models that might account for the high Pb (and Br) levels in the eclogite brines: (1) infiltration of highly saline, Pb-rich,
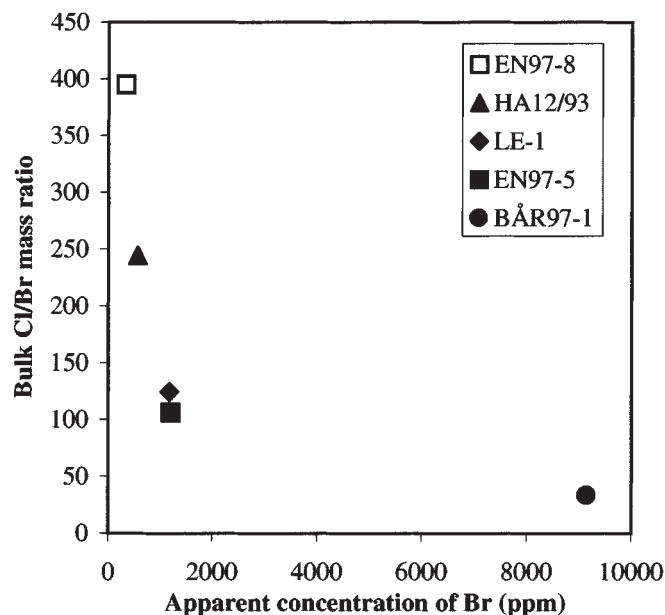

Figure 4. Bulk halogen chemistry of fluid inclusions analyzed by crush-leach method. Sample locations: En—Engebøfjellet, HA—Holsnøy, LE—Leknes, BÅR—Bårdsholmen.

eclogite-forming fluid and (2) consumption of infiltrating H_2O in a fluid with initially moderate salinity and Pb and Br concentrations by eclogite-forming hydration reactions. We cannot exclude the possibility of postentrapment leakage of the fluid inclusions, which could modify their chemistry.

Model 1 predicts that the Bårdsholmen eclogite should be Pb enriched relative to other eclogites. To test this prediction, a range of Norwegian eclogites was analyzed for Pb by XRF; all analyzed eclogites, including the Bårdsholmen eclogite, fell in the range of 5–45 ppm Pb (i.e., normal crustal Pb concentrations). It could be argued that the lack of Pb enrichment in the bulk eclogite could reflect the lack of a mechanism to precipite Pb phases from the Pb-rich fluid, but the presence of abundant sulfides (pyrite and chalcopyrite) in the Bårdsholmen and other eclogites makes that argument unlikely.

Model 2 assumes a limited fluid infiltration into the granulite complex and that the fluid was evolving toward higher salinities and lower water activities as hydration progressed. In the process, elements that were least compatible with the silicate structures and/or most strongly complexed by chloride became concentrated into the brine, while a low water activity in highly saline brines (see Aranovich and Newton, 1997) permitted appreciable partitioning of Cl (but not Br) into hydroxy-silicates. This model is strongly favored when considering the available fluid- and mineral-chemistry data from the Bårdsholmen locality. In light of these data, the higher Cl/Br ratios in fluid inclusions from the other eclogite localities suggest that the degree of external vs. internal buffering of the fluid chemistry is variable, depending upon the fluid-rock ratios and the extent of hydroxy-silicate formation.

In view of the small size of the Bårdsholmen body, it is possible that some of the Pb found in the eclogite was released from the breakdown of K-feldspar in the adjacent granulites during eclogite-facies metamorphism, as Pb may be carried in high levels in K-feldspar (generally <100 ppm). Bulk-Pb XRF analyses of the leucocratic granulite (comprising 58 vol% K-feldspar) and the eclogite-facies felsites (no K-feldspar) gave 30 ppm Pb and 10 ppm Pb, respectively (average values). This result implies that 20 ppm Pb was lost from the leucocratic granulites during metamorphism, i.e., about 50 g of Pb per cubic meter of leucocratic granulite.

CONCLUSIONS

This work documents the presence of high Pb and Br concentrations in eclogite-facies brines from western Norway. Extreme Pb, Cl, and Br enrichment is likely the consequence of partitioning into a dwindling amount of fluid during eclogite-forming hydration. Bulk fluid-inclusion chemistry data indicate that because the halogens did not behave conservatively (i.e., remain solely in the fluid) during metamorphism, Cl-Br fractionation complicates the use of halogens as tracers for metamorphic fluid sources. Breakdown of K-feldspar in adjacent gneisses during eclogite-facies metamorphism may have released Pb into the fluid phase.

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