Serpenitization of abyssal peridotites is known to produce extremely reducing conditions as a result of dihydrogen (H$_2$aq) release upon oxidation of ferrous iron in primary phases to ferric iron in secondary minerals by H$_2$O. We have compiled and evaluated thermodynamic data for Fe–Ni–Co–O–S phases and computed phase relations in fO$_2$, fS$_2$, and aH$_2$aq–aH$_2$S$_2$aq diagrams for temperatures between 150 and 400°C at 50 MPa. We use the relations and compositions of Fe–Ni–Co–O–S phases to trace changes in oxygen and sulfur fugacities during progressive serpentinization and stabilization of peridotites from the Mid-Atlantic Ridge in the 15°20’N Fracture Zone area (Ocean Drilling Program Leg 209). Petrographic observations suggest a systematic change from awaruite–magnetite–pentlandite and heazlewoodite–magnetite–pentlandite assemblages forming in the early stages of serpentinization to millerite–pyrite–polydymite-dominated assemblages in steatized rocks. Awaruite is observed in all brucite-bearing partly serpentinized rocks. Apparently, buffering of silica activities to low values by the presence of brucite facilitates the formation of large amounts of hydrogen, which leads to the formation of awaruite. Associated with the prominent desulfurization of pentlandite, sulfide is removed from the rock during the initial stage of serpentinization. In contrast, stabilization indicates increased silica activities and that high-sulfur-fugacity sulfides, such as pyrite–vaesite solid solution, form as the reducing capacity of the peridotite is exhausted and H$_2$ activities drop. Under these conditions, sulfides will not desulfurize but precipitate and the sulfur content of the rock increases.

The co-evolution of fO$_2$, fS$_2$, and aH$_2$aq in the system follows an isopotential of H$_2$S$_2$aq, indicating that H$_2$S in vent fluids is buffered. In contrast, H$_2$ in vent fluids is not buffered by Fe–Ni–Co–O–S phases, which merely monitor the evolution of H$_2$ activities in the fluids in the course of progressive rock alteration. The co-occurrence of pentlandite–awaruite–magnetite indicates H$_2$S$_2$aq activities in the interacting fluids near the stability limit of water. The presence of a hydrogen gas phase would add to the catalyzing capacity of awaruite and would facilitate the abiotic formation of organic compounds.

**KEY WORDS:** serpentinization; ODP Expedition 209; sulfide; oxygen fugacity; sulfur fugacity; hydrothermal system; metasomatism; Mid-Atlantic Ridge

**INTRODUCTION**

Mantle peridotite is commonly exposed at the seafloor of ultraslow- and slow-spreading mid-ocean ridges by detachment faulting that initiated close to the spreading axes (e.g. Cann et al., 1997; Tucholke et al., 1998). Retrograde metamorphic hydration of these rocks as a result of reaction with seawater (i.e. serpentinization) is widespread in these settings. Serpentinization strongly influences the rheology of the oceanic lithosphere (Escartin et al., 1997), the geochemical budgets of the oceans (Thompson & Melson; 1970; Snow & Dick, 1995), and microbial processes within, at, and above the seafloor (Alt & Shanks, 1998; O’Brien et al., 1998; Kelley et al., 2001). A remarkable feature of serpentinization is the strongly reducing nature of the interacting fluids, as indicated by the occurrence of native metals or alloys in serpentinites (Nickel, 1959; Chamberlain et al., 1965; Lorand, 1985; Abrajano & Pasteris, 1989). Fluids issuing from ultramafic massifs, for instance in the Coast Range and Samail ophiolites, exhibit exceptionally high concentrations of dissolved dihydrogen (H$_2$aq) (Thayer, 1966; Barnes et al., 1967; Neal & Stanger, 1983). Serpentine-hosted seafloor hydrothermal systems also show high H$_2$aq concentrations of 10–15 mmol/kg.
and many other phases, however, were not considered in previous theoretical studies dealing explicitly with seafloor hydrothermal systems because of a scarcity of thermodynamic data. To overcome these difficulties, we added thermodynamic data for some crucial phases of the Fe–Ni–Co–O–S system to the SUPCRT92 (Johnson et al., 1992) database and created a new EQ3/6 (Wolery, 1992) isobaric isobaric/isochoric (50 MPa) thermodynamic database for temperatures from 0 to 400°C in 25°C increments. Values of the dissolution reaction constant (log K) for phases for which heat capacity data are unavailable were estimated using the van't Hoff relation. Our approach is to document carefully Fe–Ni–Co–O–S phase relations in altered peridotites from the Ocean Drilling Program (ODP) Leg 209, Mid-Atlantic Ridge (MAR) 15°N area, and determine phase stabilities in the aH2Oaq–aH2S,aq plane. Following Frost (1985), we use these phase relations to deduce the evolution paths of peridotite–water interaction. Our goal is to estimate H2Oaq and H2S,aq concentrations in fluids associated with the assemblages observed so as to compare the predicted concentrations with those measured in field and experimental studies (Seyfried & Dibble, 1980; Janecky & Seyfried, 1986; McCollom & Seewald, 2001; Charlou et al., 2002; Douville et al., 2002; Allen & Seyfried, 2003; Proskurowski et al., 2006; Seyfried et al., 2007).

### GEOLOGICAL SETTING

The area of the 15°20’N Fracture Zone (FZ, Fig. 1) at the slow-spreading (<3 cm/year, full rate) MAR has been

### Table 1: Idealized formulae of opaque minerals in serpentined peridotites

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>awaruite</td>
<td>Ni3Fe</td>
</tr>
<tr>
<td>tetrataenite</td>
<td>NiFe</td>
</tr>
<tr>
<td>pentlandite</td>
<td>(FeNi)2S</td>
</tr>
<tr>
<td>godlevskite</td>
<td>Ni3S</td>
</tr>
<tr>
<td>heazlewoodite</td>
<td>Ni3S</td>
</tr>
<tr>
<td>millerite</td>
<td>NiS</td>
</tr>
<tr>
<td>violanite</td>
<td>Ni3S</td>
</tr>
<tr>
<td>pyrite</td>
<td>Ni2S</td>
</tr>
<tr>
<td>pyrrhotite</td>
<td>FeS</td>
</tr>
<tr>
<td>linnaeite</td>
<td>Co3S</td>
</tr>
<tr>
<td>cattierite</td>
<td>CoS</td>
</tr>
<tr>
<td>jaipurite</td>
<td>CoFe</td>
</tr>
<tr>
<td>wairauite</td>
<td>CuFeS2</td>
</tr>
<tr>
<td>chalcopyrite</td>
<td></td>
</tr>
</tbody>
</table>
explored in detail by numerous surveys (e.g. Rona et al., 1987; Bougault et al., 1988; Cannat et al., 1997; Casey et al., 1998; Escartin & Cannat, 1999; Escartin et al., 2003; Fujiwara et al., 2003). Basaltic volcanism is sparse north of the 14°N region and the volcanic rocks are mainly enriched-type mid-ocean ridge basalts (E-MORB) (Dosso & Bougault, 1986; Dosso et al., 1993). Two magmatic centers at 14° and 16°N coincide with negative mantle Bouguer gravity anomalies, whereas the region between these gravity bull's-eyes shows a gravity high consistent with the predominance of mantle rocks at the seafloor (e.g. Cannat et al., 1997; Escartin & Cannat, 1999; Fujiwara et al., 2003). Extensive outcrops of serpentinized peridotites and gabbroic rocks on both rift flanks are indicative of a heterogeneous lithosphere, a high ratio of tectonic to magmatic extension, crustal thinning and the formation of oceanic core complexes along long-lived low-angle detachment faults (Escartin & Cannat, 1999). ODP Leg 209 drilled 19 holes at eight sites north and south of the 15°20’N FZ into variably serpentinized peridotites intruded by gabbroic rocks (Kelemen et al., 2004a, 2007). The following brief description of drill holes and rock alteration is based on the work of Kelemen et al. (2004a) and Bach et al. (2004), and focuses on those holes from which samples were selected for this study.

Hole 1268A lies on the western rift valley wall south of the 15°20’ FZ and extends 147.6 m into completely altered harzburgite, dunite, strongly altered late magmatic dikes and mylonitic shear zones. The rocks were affected by pervasive serpentinization and locally a superimposed pervasive replacement of serpentine by talc (steatitization). Sulfides are abundant in particular in the lower half of the section.

Site 1270 is the southernmost of all the drill sites, located on the eastern flank of the MAR in the vicinity of the Logatchev hydrothermal field (14°45’N) on the eastern median valley wall. Peridotites from Hole 1270C are pervasively serpentinized and steatized adjacent to gabbroic veins. Although alteration of peridotites from Holes 1270C and 1270D mainly took place under static conditions, some peridotites are closely related to strongly deformed, schlieren-like gabbroic intrusions that have been completely altered to chlorite and tremolite. In addition, Holes 1270C and 1270D contain minor carbonate and oxide veins.

Site 1271 is located on the inside corner high of the MAR spreading segment south of the 15°20’ FZ. Drill core 1271A is mainly composed of completely serpentinized dunite. Drill core 1271B comprises variably serpentinized dunite and harzburgite. Steatitization is minor in these rocks.

Site 1274 is located 31 km north of the 15°20’N FZ on the western rift valley wall at 3940 m water depth and ~700 m west of the termination of the detachment fault. Hole 1274A penetrates 156 m into the basement and recovered 35 m of core that comprises 77% harzburgite, 20% dunite, and 3% gabbro. Peridotite from this hole represents the least altered rock from Leg 209 with up to 33% of the original minerals preserved. For a comprehensive description of all the drill sites and a more detailed description of the alteration mineralogy and chemistry we refer the reader to Kelemen et al. (2004a, 2007), Bach et al. (2004, 2006) and Paulick et al. (2006).
ANALYTICAL METHODS

Microscopy and electron microprobe analysis

Thin sections were optically investigated in transmitted and reflected light using a Leica DM RXP HC oil immersion microscope. Mineral compositions were analyzed with a JEOL Superprobe JXA 8900 R electron microprobe at the University of Kiel (Germany), equipped with five wavelength-dispersive spectrometers. Minerals were analyzed with an accelerating voltage of 20 kV for a beam current of 20 nA and a fully focused 1 μm beam diameter. Both synthetic and natural mineral standards were used. The raw data were corrected using the ZAF method. Micro-scale element mapping and backscattered electron images of serpentine meshes and nickeliferous opaque mineral assemblages were used to complement petrographic observations. In total, 915 single point analyses of nickeliferous opaque minerals were obtained. Although many of these analyses had low totals because of the small grain size of most of the Fe–Ni–Co–O–S minerals, their evaluation helped us understand the changing phase relations with progressive serpentinization.

Thermodynamic calculations

Thermodynamic calculations were conducted using the SUPCRT92 (Johnson et al., 1992) computer code. The database of SUPCRT92 consists of standard-state (298.15 K and 10^5 Pa) thermodynamic parameters, Maier–Kelley coefficients, and equation of state parameters for pure minerals, aqueous species and gases for the calculation of equilibrium constants (log K values) for temperatures and pressures up to 1000°C and 500 MPa. The database used for this study combines all upgrades from the slop98.dat and the speq02.dat database (Wolery & Jove-Colon, 2004). Phase diagrams were constructed using Geochemist’s Workbench® (GWB®) version 7.02 (Bethke, 2007). A thermodynamic database for GWB® was assembled for a pressure of 50 MPa and temperatures of 0, 25, 100, 200, 250, 300, 350, and 400°C. Log K values in that database were either computed by SUPCRT92 or calculated using a van’t Hoff temperature extrapolation, while ignoring the effect of pressure (see below). Log K values for the dissolution of minerals are given in Table 2. Activity coefficients for H₂S,aq were calculated following Drummond (1981) for CO₂,aq, whereas the activity coefficient for H₂S,aq was assumed to be unity at all temperatures (see Helgeson et al., 1970). Actual fugacity–concentration relations for H₂S and H₂ from Kishima (1989) and Kishima & Sakai (1984) suggest some deviation from ideal behavior. However, corrections to the log K values for equilibrium between dissolved and gaseous species were not applied, because (1) fugacity–concentration relations are unavailable for T < 300°C and (2) corrections are negligible (<0.15 log units) between 300 and 400°C.

In the following subsections, we describe the thermodynamic data for the Fe–Ni–Co–O–S phases, which are not part of the SUPCRT92 mineral set. Uncertainties in these data and their propagation in the calculation of phase boundaries are hard to quantify. Standard state thermodynamic data for minerals, aqueous and gaseous species, as well as high-temperature heat capacity data for minerals and interaction parameter for solid solutions are often poorly known. Consequently, these data must be considered preliminary.

Pentlandite

Berezovskii et al. (2001) conducted low-temperature heat capacity measurements for synthetic pentlandite (Fe₄₆₀Ni₃₄₀S₈₀) and reported a standard entropy (S°) of 474.9 J/mol per K and H°₂₉₈.₁₅ − H₀ of 762.80 kJ/mol. Using these data, we calculated a standard enthalpy of formation (ΔH°₂₉₈.₁₅) of −847.0 kJ/mol for stoichiometric pentlandite (Fe₄₃₃Ni₃₁₈S₈₀) using standard enthalpies of formation for troilite (FeS) and millerite (NiS) from Robie & Hemingway (1995). Cemicˇ & Kleppa (1987) reported a ΔH°₂₉₈.₁₅ of −837.37 ±14.59 kJ/mol, which is in agreement with our results. An apparent Gibbs energy of formation (ΔG°₂₉₈.₁₅) of −836.3 kJ/mol was derived using the standard molar entropies of Fe, Ni and S given by Robie & Hemingway (1995). This number is consistent with ΔG°₂₉₈.₁₅ = −835.2 kJ/mol from Craig & Naldrett (1971). Because high-temperature heat capacity data are lacking, we used the van’t Hoff extrapolation and SUPCRT92 data for Fe, Ni and S to compute log K values for dissolution of pentlandite. A molar volume (V°) of 153.3 cm³/mol was calculated for a natural pentlandite from cell constants given by Kouvo et al. (1959).

Heazlewoodite

ΔG°₂₉₈.₁₅, ΔH°₂₉₈.₁₅ and S° for heazlewoodite (Ni₃S₂) were taken from Robie & Hemingway (1995). We used high-temperature heat capacity data from Stolten et al. (1991) to calculate Maier–Kelley coefficients. V° (40-655 cm³/mol) for heazlewoodite was calculated using cell constants given by Parise (1980).

Awaruite

Howald (2003) reported ΔG°₂₉₈.₁₅, ΔH°₂₉₈.₁₅ and S° for awaruite (Ni₃Fe). We calculated log K values for awaruite by means of the van’t Hoff extrapolation and SUPCRT92 data for Fe and Ni, because high-temperature calorimetric data are unavailable. V° (26-96 cm³/mol) was calculated from cell constants given by Anthony et al. (1990).

Tetraetaenite

Howald (2003) also reported ΔG°₂₉₈.₁₅, ΔH°₂₉₈.₁₅ and S° for tetraetaenite (NiFe). We calculated log K values for tetraetaenite by means of the van’t Hoff extrapolation and SUPCRT92 data for Fe and Ni, because high-temperature calorimetric data are unavailable. V° (28-58 cm³/mol) was calculated from cell constants given by Anthony et al. (1990).
Table 2: Equilibrium constants for dissolution of opaque minerals ($P = 50$ MPa)

<table>
<thead>
<tr>
<th>Reaction no.</th>
<th>Mineral</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$0^\circ C$</td>
</tr>
<tr>
<td>1</td>
<td>awaruite</td>
<td>231.70</td>
</tr>
<tr>
<td>2</td>
<td>tetrataenite</td>
<td>119.43</td>
</tr>
<tr>
<td>3</td>
<td>pentlandite</td>
<td>−57.71</td>
</tr>
<tr>
<td>4</td>
<td>heazlewoodite</td>
<td>30.68</td>
</tr>
<tr>
<td>5</td>
<td>godlevskite</td>
<td>−87.45</td>
</tr>
<tr>
<td>6</td>
<td>millerite</td>
<td>−9.13</td>
</tr>
<tr>
<td>7</td>
<td>polydymite</td>
<td>−121.00</td>
</tr>
<tr>
<td>8</td>
<td>violarite</td>
<td>−118.14</td>
</tr>
<tr>
<td>10</td>
<td>Waialuaite</td>
<td>120.48</td>
</tr>
<tr>
<td>11</td>
<td>cobaltpentlandite</td>
<td>−82.22</td>
</tr>
<tr>
<td>12</td>
<td>jaipurite</td>
<td>−8.25</td>
</tr>
<tr>
<td>13</td>
<td>linnaeite</td>
<td>−112.41</td>
</tr>
<tr>
<td>14</td>
<td>catterlrite</td>
<td>−17.94</td>
</tr>
<tr>
<td>15</td>
<td>H$_2$Saq</td>
<td>−7.28</td>
</tr>
<tr>
<td>16</td>
<td>H$_2$Oaq</td>
<td>−50.66</td>
</tr>
</tbody>
</table>

Reaction no.

1. Ni$_3$Fe + 8 H$^+$ + 2 O$_2$aq = 3 Ni$^{2+}$ + Fe$^{2+}$ + 4 H$_2$O
2. NiFe + 4 H$^+$ + O$_2$aq = Fe$^{2+}$ + Ni$^{2+}$ + 2 H$_2$O
3. Fe$_4$Ni$_4$S$_8$ + 10 H$^+$ = 4 Fe$^{2+}$ + 4 Ni$^{2+}$ + 8 HS$^-$ + H$_2$O
4. Ni$_5$S$_8$ + 4 H$^+$ + 0.5 O$_2$aq = 3 Ni$^{2+}$ + 2 HS$^-$ + H$_2$O
5. Ni$_5$S$_8$ + 10 H$^+$ = 9 Ni$^{2+}$ + 8 HS$^-$ + H$_2$O
6. NiS + H$^+$ = Ni$^{2+}$ + HS$^-$
7. Ni$_5$S$_4$ + 4 H$^+$ = Ni$^{2+}$ + 2 Ni$^{2+}$ + 4 HS$^-$
8. FeNi$_5$S$_8$ + 4 H$^+$ = Fe$^{2+}$ + 2 Ni$^{2+}$ + 4 HS$^-$
9. NiS$_2$ + H$_2$aq = Ni$^{2+}$ + 2 HS$^-$
10. CoFe + 4 H$^+$ + O$_2$aq = Fe$^{2+}$ + Co$^{2+}$ + 2 H$_2$O
11. Co$_3$S$_8$ + 10 H$^+$ = 9 Co$^{2+}$ + 8 HS$^-$ + H$_2$O
12. CoS + H$^+$ = Co$^{2+}$ + HS$^-$
13. Co$_3$S$_4$ + 4 H$^+$ = Co$^{2+}$ + 2 Co$^{2+}$ + 4 HS$^-$
14. Co$_2$S$_2$ + H$_2$aq = Co$^{2+}$ + 2 HS$^-$
15. H$_2$Saq = HS$^-$ + H$^+$
16. H$_2$Oaq = H$_2$O + 0.5 O$_2$aq

Data are lacking $V^\circ$ (13.84 cm$^3$/mol) was calculated from cell constants given by Albertsen et al. (1978).

**Godlevskite**

Thermodynamic properties of godlevskite (Ni$_5$S$_8$) were obtained from heat capacity measurements by Stoll et al. (1994) for Ni$_7$S$_6$ and Ni$_5$S$_4$. A $\Delta H^\circ_f$ of −802.92 kJ/mol was calculated from $H_{298.15}$ − $H_0$ (7.920 kJ/mol) using the standard enthalpy of formation of NiS given by Robie & Hemingway (1995). $G^\circ_f$ for a natural godlevskite (148.7 cm$^3$/mol) was calculated from cell constants given by Fleet (1987).

**Millerite**

The standard state thermodynamic properties of millerite (NiS) were taken from Robie & Hemingway (1995). The transition of $\beta$-millerite at 379°C to $\alpha$-millerite was...
accounted for in the calculation of the equilibrium constants at 400°C.

**Vaesite**

$\Delta H^0$, $S^0$, and heat capacity data for vaesite (NiS$_2$) were taken from NIST (Chase, 1998). $\Delta G^0_f$ ($-291.8$ kJ/mol) was derived using $\Delta H^0_f$ and the standard molar entropies of Ni and S. $V^0$ was taken from Smyth & McCormick (1995).

**Violarite**

We used $\Delta G^0_f$ and $S^0$ of violarite (FeNi$_2$S$_4$) reported by Craig (1971). $\Delta H^0_f$ was taken from Cemič & Kleppa (1987). As no heat capacity data are available we calculated log $K$ values for dissolution of violarite using the van't Hoff extrapolation and SUPCRT92 data for Fe, Ni and S. $V^0$ was taken from Smyth & McCormick (1995).

**Polydymite**

$\Delta H^0_f$, $S^0$, and heat capacity data for polydymite (Ni$_3$S$_4$) were taken from NIST (Chase, 1998). $\Delta G^0_f$ ($-291.8$ kJ/mol) was derived using standard molar entropies of Ni and S given by Robie & Hemingway (1995). $V^0$ was taken from Smyth & McCormick (1995).

**Cobaltpentlandite**

$\Delta H^0_f$ (854.79 kJ/mol) and $S^0$ (463.17 J/mol per K) data for the Co-endmember (Co$_9$S$_8$) of the pentlandite solid solution series were taken from Rosenqvist (1954). $\Delta G^0_f$ (836.43 kJ/mol) was computed using $\Delta H^0_f$ and standard molar entropies for Co and S given by Robie & Hemingway (1995). High-temperature heat capacity data were adopted from Kelley (1949). The standard molar volume (147.1 cm$^3$/mol) was calculated using cell parameters from Bayliss (1990).

**Wairauite**

$\Delta G^0_f$ and $\Delta H^0_f$ for wairauite (Co$_3$Fe) are listed in the scientific group thermodata binary compounds database (Dinsdale, 1991). We calculated dissolution constants by means of the van't Hoff extrapolation and SUPCRT92 data for Co and Fe. The molar volume (140.9 cm$^3$/mol) was calculated from cell constants given by Bayliss (1990).

**Linnaeite, cattierite, and jaipurite**

$\Delta H^0_f$, $S^0$, and high-temperature heat capacity data for all three phases were taken from Mills (1974). The $\Delta G^0_f$ of all three minerals was calculated using $\Delta H^0_f$ and standard molar entropies for Co and S given by Robie & Hemingway (1995). The molar volumes of linnaeite (Co$_9$S$_8$) and cattierite (Co$_9$S$_8$) were taken from Robie & Hemingway (1995), and that of jaipurite (CoS) from Naumov et al. (1974).

**RESULTS**

**Petrography**

We distinguish two types of rock alteration: serpentinization of peridotite and steatitization of serpentinite. At Site 1274, peridotites are partially to fully serpentinized, whereas at Sites 1270, 1271 and 1268, partially to fully serpentinized peridotites have undergone additional steatitization to variable degrees (see Bach et al., 2004). Microtextures of the serpentinized peridotites range from pseudomorphic mesh and hourglass textures after olivine to transitional ribbon texture to non-pseudomorphic and interlocking textures. Typical in partially serpentinized rocks (65–98% altered) are mesh-textures with fresh olivine relics in the mesh centers and serpentinite/brucite-rich mesh rims. Magnetite is concentrated away from the olivine kernels along former grain boundaries in areas of complete serpentinization (e.g. Bach et al., 2006). Completely serpentinized rocks have serpentine/brucite/iowaiite centers, which often appear dark in transmitted light. Most samples are extensively veined by paragranular and transgranular serpentine veins. Paragranular veins form an anastomosing network that is usually foliation parallel and wraps around porphyroclasts, whereas transgranular veins crosscut porphyroclasts (Kelemen et al., 2004a). Late isotropic picrolite veins are also transgranular. Serrate chrysotile veins occur almost exclusively in non-pseudomorphic interlocking textures. In proximity to gabbroic intrusions steatitization is strongest and often invades adjacent serpentine by replacing former transgranular serpentine veins. Even in strongly steatitized rocks the original serpentine micro-texture is commonly preserved, indicating alteration under static conditions (Bach et al., 2004). Cr-spinel is widespread but is clearly a magmatic relict that, as mentioned by Eckstrand (1975), serves only as a nucleus to secondary overgrowth of magnetite. Incipient alteration of Cr-spinel is indicated by occasional overgrowths of grains by a thin (5–10 μm) ferrit-chromite rim.

The following petrographic description focuses on opaque mineral assemblages in variably serpentinized and steatitized peridotites. Because of the small grain size of most nickeliferous opaque minerals, their identification by reflected light microscopy was often impossible. To overcome this problem and to document better the changing Fe–Ni–Co–O–S phase relations with progressive serpentinization we analyzed the chemical compositions of opaque phases by electron microprobe and used the compositional data for phase identification.

**Primary sulfides**

Peridotites from ODP Leg 209 are strongly melt-depleted as indicated by their modal and trace element composition (Paulick et al., 2006; Seyler et al., 2007). Intercumulus sulfide–oxide ‘blebs’ of clear magmatic origin, as described by Eckstrand (1975) for the Dumont serpentinite, or sulfide
inclusions hosted by olivine or pyroxene, as described by Lorand (1989), were not recognized in samples investigated here.

Primary sulfides are commonly completely replaced by secondary sulfides or alloys formed during serpentinization. Seyler et al. (2007) reported local occurrences of magmatic sulfides (polyhedral blebs of pentlandite, bornite, and chalcopyrite with concave inward grain boundaries) probably introduced during late melt impregnation of the lithospheric mantle. Chalcopyrite was found only in samples from Site 1268; no Cu-sulfides were present in the limited number of samples investigated from Sites 1270, 1271, and 1274. Sulfide grains residual to melting in ultrafase rocks often consist of pentlandite and minor pyrrhotite. Although pyrrhotite occurs in many serpentinized peridotites described in the literature (e.g. Shiga, 1987; Abrajano & Pasteris, 1989; Lorand, 1989), it is absent in all the samples we investigated from Leg 209. Miller (2007) reported the occurrence of pyrrhotite together with pentlandite in samples from Hole 1268A. This paragenesis is probably of magmatic origin and related to gabbro intrusions frequently found in the lower part of this hole. Rare euhedral pentlandite grains with octahedral cleavage (10–30 μm in diameter), which were found in samples from Site 1271 (Figs. 2a and c), may also be primary. They usually occur in porphyroclasts of former orthopyroxene (bastite), but no pentlandite inclusions were found in fresh pyroxene.

Secondary opaque phases

The investigated serpentinites contain <0.1 vol.% nickeliferous opaque minerals. The principal opaque minerals in partly serpentinized peridotites include, in order of decreasing abundance, magnetite, cobaltian pentlandite, pentlandite, and heazlewoodite. Awaruite is common but occurs only in minor amounts. In general, nickeliferous opaque minerals appear as finely disseminated grains in the serpentine matrix. Their grain size ranges from <1 to 50 μm. By far the most abundant mineral assemblages are pentlandite + awaruite + magnetite and pentlandite + heazlewoodite + magnetite (Figs. 2b and f).

Mesh rims

In pseudomorphic serpentine mesh rims, disseminated opaque phases are generally <1 μm in diameter and thus their mineralogy could not be determined by reflected light oil immersion microscopy or conventional quantitative electron microprobe analysis. Semi-quantitative micro-scale element mapping revealed the presence of magnetite, pentlandite, heazlewoodite, and minor awaruite (the presence of awaruite could only be deduced by strong enrichments in Ni in places with low sulfur). In completely serpentinized areas magnetite forms threads along former olivine grain boundaries or pre-serpentinization intra-grain cracks.

Veins

In paragranular serpentine veins, abundant anhedral to weakly subhedral magnetite is aligned along tracks of a few tens of micrometers thickness, which are up to several hundred micrometers long. Pentlandite, heazlewoodite, awaruite, and godlevskite are preferentially located in the central part of the veins together with magnetite. In places pentlandite + awaruite + magnetite and cobaltian pentlandite + awaruite + magnetite occur in the same vein. In larger transgranular (isotropic picrolite) veins, typically 0.5–1 mm thick, magnetite occurs as either patchy single tracks or as double tracks discontinuously along both sides of the vein. In transgranular veins, nickeliferous opaques and their different replacement products are easily identified, because their grain size is typically larger (up to 50 μm in diameter) than in meshes or paragranular veins.

In transgranular veins of partly serpentinized peridotites pentlandite is often intergrown with awaruite and mantled by magnetite, suggesting that pentlandite and awaruite perhaps grew in equilibrium and were subsequently mantled by magnetite (Fig. 2d). In other cases, pentlandite is clearly replaced by awaruite and magnetite (Fig. 2b). This is indicated by the elevated Co and Ni contents of the magnetite (see below), mantling pentlandite. Remarkably, awaruite and not wairauite replaces cobaltian pentlandite. Pentlandite is frequently associated with heazlewoodite and/or magnetite (Figs. 2f and g). In some apparently pure heazlewoodite–magnetite assemblages in transgranular veins of almost fully serpentinized peridotites micro-scale element mapping revealed the presence of relic cobaltian pentlandite. It occurs as inclusions typically smaller than 1 mm within relatively coarse-grained heazlewoodite or between heazlewoodite and magnetite, suggesting that heazlewoodite and magnetite grew at the expense of cobaltian pentlandite. Heazlewoodite co-occurring with godlevskite and magnetite may also contain small cobaltian pentlandite inclusions, which are lacking in godlevskite. This indicates that godlevskite did not directly grow at the expense of cobaltian pentlandite. Because godlevskite is exclusively found in fully serpentinized rocks, it is more likely that godlevskite replaces heazlewoodite (Fig. 2h) in the final stage of serpentinization. In some completely serpentinized peridotites from Hole 1268A magnetite in veins is partially replaced by pyrite.

Bastite

Serpentine veins crossing bastite (serpentine pseudomorphic after pyroxene) are devoid of magnetite. In contrast to pentlandite co-occurring with awaruite and/or magnetite, the pentlandite occurring as a solitary phase in bastite exhibits a distinct octahedral cleavage (Fig. 2a). Where serpentinization is advanced, pentlandite in veins crossing bastite is rimmed by and/or intergrown with
Fig. 2. Back-scattered electron images of representative sulfide, oxide, and native metal assemblages in variably serpentinized and steatized peridotite samples from ODP Leg 209. (a) Pentlandite in bastite serpentine with an octahedral cleavage (sample 1271B-7R1-15; scale bar 5 μm). (b) Grain of cobaltian pentlandite (medium grey) located in a paragranular vein, partly altered to awaruite (light grey) and magnetite (dark grey) (sample 1274A-15R1-106; scale bar 10 μm). (c) Euhedral grain of cobaltian pentlandite (medium grey) intergrown with and rimmed by awaruite (light grey), located in a transgranular vein crosscutting bastite serpentine (sample 1274A-17R1-129; scale bar 3 μm). (d) Pentlandite (medium grey) intergrown with awaruite (light grey) and mantled by magnetite (dark grey) located in a transgranular serpentine vein of sample 1274A-10R1-3 (scale bar 10 μm). (e) Euhedral grain of cobaltian pentlandite in bastitic serpentine with flame-like appendages on each corner (sample 1274A-18R1-83; scale bar 3 μm). (f) Pentlandite (medium grey) and heazlewoodite (light grey) rimmed by magnetite (dark grey) in sample 1271B-7R1-98 (scale bar 10 μm). (g) Heazlewoodite (light grey) and magnetite (medium grey) in a transgranular vein of sample 1274A-20R1-126 (scale bar 10 μm). (h) Grain of heazlewoodite (light grey), which is partly replaced by godlevskite (medium grey) and mantled by magnetite (dark grey) (sample 1271B-7R1-15; scale bar 10 μm). (i) Porous polydymite that has completely replaced pentlandite associated with magnetite (sample 1271B-7R1-15; scale bar 50 μm). (j) Grain of heazlewoodite (light grey), godlevskite (light to medium grey), millerite (medium grey), and magnetite (dark grey), which hosts millerite and polydymite-s (sample 1268A-20R1-6; scale bar 100 μm). (k) Opaque vein crosscutting partly talc altered bastitic serpentine along pseudomorphic cleavage plane. Magnetite (dark grey) is in sharp contact with pyrite (medium grey), which hosts millerite and polydymite-s (sample 1268A-20R1-6; scale bar 100 μm).
awaruite (Fig. 2c), suggesting that awaruite replaced pentlandite. Awaruite in bastite is exclusively found in association with pentlandite.

**Steatitization**

Serpentine veins host magnetite that is gradually transformed to pyrite with increasing degree of steatitization (Fig. 2k). Completely steatized rocks contain pyrite, which is locally replaced by hematite and/or goethite (see Alt et al., 2007). Awaruite, pentlandite, heazlewoodite, and godlevskite are relics of serpentinization and scarce in partly steatized rocks (e.g. Fig. 2j). Where present, they are mantled by magnetite, protecting them from reaction to millerite or other higher sulfur-fugacity phases. Relics of the assemblage pentlandite + awaruite + magnetite are found in partly serpentinized peridotites that have undergone steatitization, whereas relics of the assemblages pentlandite + heazlewoodite + magnetite and pentlandite + godlevskite + magnetite were found in fully serpentinized peridotites that have undergone steatitization. With increasing degree of steatitization, sulfur-poor Ni sulfides are progressively replaced by sulfur-rich Ni sulfides (Figs. 2i–k). Millerite is the most abundant Ni sulfide in partly steatitized samples, where it replaces heazlewoodite or godlevskite. Where steatitization is advanced, minerals of the violarite–polydymite solid solution (polydymite-ss) grow at the expense of pentlandite or millerite and magnetite (Figs. 2i and k). In completely steatitized serpentinites magnetite is completely replaced by pyrite. Chalcopyrite is absent in samples from Sites 1270, 1271 and 1274. It occurs only within a few steatitized samples from Hole 1268A together with pyrite. Miller (2007) found chalcopyrite associated with pyrrhotite or minerals from the monosulfide solid solution in samples from the lower half of Hole 1268A, but the occurrence of these minerals is clearly related to gabbroic intrusions.

**Relations with increasing degree of serpentinization and steatitization**

The assemblage type changes with increasing extent of serpentinization (Table 2). Pentlandite + awaruite + magnetite is exclusively found in partly serpentinized peridotites, whereas pentlandite + heazlewoodite + magnetite is usually found in fully serpentinized peridotites. The assemblages pentlandite + awaruite (in bastite), magnetite + heazlewoodite, and heazlewoodite + godlevskite + magnetite (in fully serpentinized rocks) are common, but less abundant (Fig. 2c, g and h). Locally, pentlandite occurs as a solitary phase (Fig. 2a). All examined samples lack cobaltian minerals other than cobaltian pentlandite (and catterite in pyrite; see below). The sulfur-rich Ni sulfides developed exclusively in steatitized rocks are millerite, vaesite (in pyrite; see below), and minerals of the polydymite-ss. Pyrite replacing magnetite veins was found in some fully serpentinized samples from Hole 1268A. These pyrite-bearing serpentinites show the first signs of steatitization, preferentially of bastite. The assemblages observed change with increasing extent of serpentinization from pentlandite + awaruite + magnetite to pentlandite + heazlewoodite + magnetite to heazlewoodite + godlevskite + magnetite, and continue to change with progressive steatitization manifested in Hole 1268A to magnetite + pyrite + millerite (magnetite + pyrite, if Ni is locally lacking) to pyrite + millerite + polydymite-ss to pyrite + polydymite-ss (to pyrite + vaesite as indicated by chemical analyses; see below).

**Mineral chemistry**

**Awaruite**

In partly serpentinized peridotites from Hole 1274A the Ni and Fe contents of awaruite vary between 63-0 and 73.5 mol % and 21.3 and 29.3 mol %, respectively (Supplementary Data Table A1 at http://petrology.oxfordjournals.org/). Co is present only in minor amounts, usually <3-5 mol %. In one sample from Hole 1274A an awaruite grain has an elevated copper content of 2-8 mol %; in all other awaruite grains the copper concentration was below the detection limit of the electron microprobe (~300 ppm). Awaruite is scarce in Hole 1268A and has Ni contents ranging from 64-0 to 71.5 mol %. The Fe content varies between 26-0 and 27.9 mol % and, although generally a minor constituent, Co contents can range up to 6-6 mol %. Awaruite is absent in samples from Hole 1271B. Compositional variability of awaruite seems to be independent of pentlandite composition, as the Co content is rather uniform and Ni/Fe atomic ratios of awaruite exhibit no systematic relation with pentlandite composition. Wairauite (CoFe) was described by Chamberlain et al. (1965) and Abrajano & Pasteris (1989) in serpentinites, but could not be found in the samples investigated here. The transformation of cobaltian pentlandite to awaruite suggests that the stability field of awaruite is much larger than that of wairauite.

**Pentlandite**

Pentlandite displays a wide compositional range that may indicate a solid solution between Co9S8 and (FeNi)-pentlandite with approximately equal proportion of both metals (Supplementary Data Table A2; Fig. 3). The cobalt content of pentlandite varies from virtually Co-free (<0.3 mol %) to Co-rich (≥42 mol %). The atomic metal/sulfur ratio of most pentlandite grains is close to 9/8 (i.e. 1.125). The full range, however, is between 1.06 and 1.67. Rather than real variations in pentlandite composition, the elevated ratios are related to finely intergrown awaruite or heazlewoodite in pentlandite. The slightly lower atomic metal/sulfur ratios of the pentlandite fall within the metal/sulfur range for natural pentlandites reported by Harris & Nickel (1972) and synthetic pentlandites reported by Kaneda et al. (1986). In Fig. 3 Co-rich
pentlandites from Sites 1271 and 1274 indicates temperatures below 200°C. Pentlandite forms a continuous Co₅S₈─Fe₄S₈ solid solution at temperatures above 300°C. Bimodal Co distribution in pentlandites from Sites 1271 and 1274 indicates temperatures below 200°C, whereas those from Site 1268 indicate temperatures >300°C.

The atomic metal/sulfur ratio of godlevskite ranges near stoichiometric and varies between 1.0 and 1.08 (Supplementary Data Table A4). The atomic metal/sulfur ratio of heazlewoodite is mostly 1.0-1.08, whereas millerite with high Fe content (>1.5 mol %) occurs with magnetite. Usually millerite associated with relic cobaltian pentlandite in samples from Hole 1271B has elevated Co contents of <1.1 mol %, indicating that millerite grew at the expense of cobaltian pentlandite.

The atomic metal/sulfur ratio of heazlewoodite is mostly near stoichiometric and varies between 1.4 and 1.69. Considerable amounts of Fe (<5.6 mol %) and small amounts of Co (<0.36 mol %) were detected (Supplementary Data Table A3) in heazlewoodite from Hole 1274A. However, the presence of minute inclusions of pentlandite in heazlewoodite, as mentioned above, could increase the apparent Fe and Co content, but would also lower the atomic metal/sulfur ratio systematically. Samples from Hole 1271B, however, have abundant heazlewoodite. Variable amounts of Fe (0.5–7.6 mol %) and small amounts of Co (<0.32 mol %) were detected in these grains. High Fe contents together with low totals suggest that some magnetite was included in the analyses. In contrast, where analyses approach 100 wt % higher metal/sulfur ratios are positively correlated with a higher Fe content, possibly indicating small-scale intergrowths with awaruite.

The atomic metal/sulfur ratio of godlevskite ranges between 1.08 and 1.25 (Supplementary Data Table A4). Most analyses are consistent with a stoichiometry of Ni₅S₈. Godlevskite proposed by Fleet (1987). Where godlevskite replaces heazlewoodite, metal/sulfur ratios are slightly elevated, whereas low metal/sulfur ratios correspond to godlevskite associated with millerite. Common impurities in godlevskite from Leg 209 are Fe and Co, ranging between 0.7 and 5.0 mol % and 0.0 and 0.8 mol %, respectively. In places elevated Fe contents correlate with low totals, suggesting that some magnetite was included in the analyses.

**Millerite**

The atomic metal/sulfur ratio of millerite (Supplementary Data Table A5) in Hole 1268A ranges between 0.97 and 1.06. Where millerite replaces godlevskite the metal/sulfur ratio is slightly elevated. The Fe content varies from 0.3 to 5.0 mol % with a bimodal distribution depending on associated minerals. Millerite with low Fe content (<1.2 mol %) is always associated with pyrite and polydymite-ss, whereas millerite with high Fe content (>1.5 mol %) occurs with magnetite. Usually millerite associated with pyrite or polydymite-ss contains some Co, but in most cases this is below 0.3 mol %. Remarkably, millerite associated with relic cobaltian pentlandite in samples from Hole 1271B has elevated Co contents of <1.1 mol %, indicating that millerite grew at the expense of cobaltian pentlandite.

**Polydymite–violarite solid solution (polydymite-ss)**

In polydymite-ss from Hole 1268A the molar metal/sulfur ratio varies between 0.72 and 0.80, whereas polydymite-ss from Hole 1271B has higher metal/sulfur ratios as a result of intergrowths with magnetite (Supplementary Data Table A6). Compositions are intermediate between polydymite and violarite, with Fe content ranging from 7.1 to 12.3 mol %. Polydymite-ss grains associated with millerite have a mean Fe content of 7.7 mol %, whereas those that occur with pyrite contain on average 11.2 mol % Fe. The Co content is mostly below 0.3 mol %, but one grain associated with millerite contains 3.7 mol % Co. Because of the porous texture of polydymite-ss (and intergrowths with magnetite in samples from Hole 1271B) most electron microprobe analyses have low totals (Supplementary Data Table A6).

**Magnetite**

Magnetite is rather uniform in composition with small amounts of NiO (see Supplementary Data Table A7; <2.9 mol %) and CoO (<0.3 mol %). Magnetite replacing cobaltian pentlandite is slightly enriched in Co and Ni compared with magnetite that is not associated with cobaltian pentlandite. Copper is below the detection limit of the electron microprobe (~300 ppm) in all magnetite analyses of rocks from Hole 1274A. For Hole 1268A magnetite analyses reveal slightly elevated copper and zinc contents (~0.05 mol %).
Pyrite
The molar metal/sulfur ratio of pyrite varies between 0.48 and 0.54 (Supplementary Data Table A8). Nickel contents in pyrite range from 0 to 7-1 mol %. The Ni content of pyrite is low if it is associated with low-Ni minerals (e.g. Co-rich pentlandite or magnetite). In contrast, the Ni content of pyrite is high if it is associated with Ni sulfides such as millerite or polydymite-ss. The majority of pyrite grains have high proportions of a vaesite component (4-8 mol %). Typical Co contents are <0.03 mol %, but can be as high as 6-1 mol % (equivalent to 18-45 mol % cattierite) in a few spots. Copper in pyrite is below the detection limit of 300 ppm.

Chalcopyrite
Chalcopyrite in t alc altered rocks from Hole 1268A exhibits a stoichiometric composition (Supplementary Data Table A9). Small amounts of Co and Ni (<0.04 mol %) were detected.

Phase diagrams
We constructed diagrams illustrating the Fe–Ni–O–S phase relations in the log fO2 vs log fS2 and log aH2Oaq vs log aH2Saq plane. Phase boundaries were all calculated for a pressure of 50 MPa, temperatures between 150 and 400°C and aH2O = 1 (Figs. 4–6). Minerals that are obviously lacking in natural samples (bunsenite, native nickel, native iron, and wustite) were omitted from the diagrams to accommodate for metastable equilibria of chemically favored minerals.

Seyfried et al. (2004) constructed an activity–activity diagram, which depicts the phase relations in the NiO–H2S–H2O–HCl system at 400°C and 50 MPa. In addition to the stability fields of the minerals considered by Seyfried et al. (2004), we show stability fields of vaesite, polydymite, godlevskite, and the Fe-bearing phases tetrataenite, awaruite and pentlandite. Violanite is metastable with respect to millerite, godlevskite, polydymite and vaesite, and therefore does not project in the phase diagrams shown. The stability region of millerite as suggested by Seyfried et al. (2004) is significantly reduced in size when pentlandite and vaesite are considered. Godlevskite is expected to be more stable over a wide range in H2aq and H2Saq activities and would exclude millerite as a stable phase. Millerite is common, however, and millerite and godlevskite even co-occur in a single opaque grain. We therefore show the phase boundaries of godlevskite as dotted lines to allow for examination of the perhaps metastable phase relations. The stability field of awaruite is larger than that of native nickel shown by Seyfried et al. (2004) and shifts the appearance of hazzlewoodite to higher H2Saq activities. Remarkably, the stability field of tetrataenite suggests that awaruite would form metastably from pentlandite. Because tetrataenite is lacking in the samples we investigated, we show the phase boundaries of tetrataenite as grey continuous lines to account for the manifested coexistence of pentlandite + awaruite + magnetite.

Log activity–activity diagrams for the Co–Fe–O–S system in the H2Oaq–H2Saq plane are shown for temperatures between 150 and 400°C at 50 MPa (Fig. 6). Because of the smaller entropy of cobaltpentlandite compared with that of pentlandite, the size of the pentlandite stability field is strongly dependent on the Co content. The higher the Co content of pentlandite the more the field expands towards lower H2aq and H2Saq activities. As awaruite and wairauite replaces cobalt pentlandite, it should be expected that the stability field of awaruite is larger than that of wairauite. This observation is in apparent contrast to the actual stable phase relations (Fig. 6). However, the greater abundance of Ni relative to Co in the system will promote the stability of nickeliferous phases relative to cobaltian phases. In addition to cobaltian pentlandite, cattierite coexisting with pyrite was the only other Co phase we detected in our samples. Jaipurite is metastable relative to cobaltian pentlandite and limnaitite, and does therefore not project.

DISCUSSION
Fe–Ni–Co–S phase relations and temperature estimates of fluid–rock interaction
The phase diagrams displayed in Figs. 4–6 indicate considerable temperature dependences of the positions of invariant points and univariant reaction lines in the H2Oaq–H2Saq activity plane. Hence, before the H2 and H2S concentrations of the interacting fluids can be estimated constraints on the prevailing temperatures of fluid–rock interaction are required. These can be estimated using phase relationships (Bach et al., 2004) or oxygen isotope compositions (Alt et al., 2007). Phase relations, specifically the replacement of olivine by serpentine, brucite and magnetite in the presence of fresh clinopyroxene from the upper half of Hole 1274A, have been interpreted to indicate low temperatures of serpentinitization (<200–250°C; Bach et al., 2004). Using whole-rock oxygen isotope data, Alt et al. (2007) estimated variable serpentinitization temperatures of peridotites from Leg 209. Consistent with the phase relation estimate, those workers proposed rather low alteration temperatures (<150°C) based on the high δ18O (up to 81‰) of samples from Hole 1274A. In contrast, higher alteration temperatures (250–350°C) are indicated by low δ18O whole-rock values (2.6–4.4‰) at Site 1268.

The phase relations in the Fe–Ni–Co–O–S system can reveal additional information about the formation temperatures (Craig, 1977; Kaneda et al., 1986; Alt & Shanks, 2003; Kitakaze & Sugaki, 2004). We investigated thin
Fig. 4. Activity–activity diagrams depicting redox phase equilibria in the Fe–Ni–O–S system from 150 to 400°C at 50 MPa. Dashed lines are the boundaries of the magnetite, hematite, pyrrhotite, and pyrite stability fields (field labels in italics); continuous lines are boundaries of awaruite, pentlandite, heazlewoodite, millerite, polydymite, and vaesite stability fields. Because the stability fields of godlevskite and tetrataenite cover the stability fields of millerite and polydymite and awaruite (in part), respectively, we show their phase boundaries as dotted and grey lines. Phase boundaries represent equal activities of the minerals in adjacent fields. In the 350°C panel, white and grey circles represent the H₂ and H₂S concentrations of fluids from the Logatchev (LHF) and Rainbow (RHF) hydrothermal fields (Charlou et al., 2002; Douville et al., 2002).
sections from the same samples, for which δ18O whole-rock data are available (Alt et al., 2007; see Table 3). The contrasting δ18O composition between rocks from Holes 1268A and 1274A is also reflected in systematic differences in Fe–Ni–O–S phase relations and mineral compositions. Both can be used in deriving rough estimates of alteration temperature. In particular, the compositions of pentlandite and polydymite-ss may reveal temperature information. Kaneda et al. (1986) reported that pentlandite forms a complete solid solution between (Fe, Ni)9S8 and Co9S8 in the 300–600°C temperature range. At 200°C, there appears to be a solvus that would allow cobaltian pentlandite to coexist with an Fe–Ni endmember pentlandite (Fig. 3). Cobaltian and non-cobaltian endmember pentlandites do indeed co-occur in veins in some samples from Hole 1274A, indicating low formation temperatures of ~200°C or lower (Supplementary Data Table A2). Whole-rock δ18O values for these samples (4.8–7.4‰, Alt et al., 2007) corroborate these rather low alteration temperatures. A single sample from Hole 1271B (10-R1-30–35) also features both pentlandites, which would seem inconsistent with alteration temperatures >350°C deduced by Alt et al. (2007) based on δ18O of rocks from Hole 1268A and similarities to rocks from Site 1271 in sulfide contents and δ34S.

Pentlandite from sample 1274A-15-R1-106–114 and most pentlandite from Hole 1268A fall just outside the 300°C range in Fig. 3. Locally, alteration temperatures may have exceeded 300°C even in Hole 1274A. Unfortunately, no δ18O data exist for that sample. All pentlandite in rocks from Hole 1268A is cobaltian so that alteration temperatures apparently were >300°C, consistent with the low δ18O values of those samples (Alt et al., 2007).

Polydymite and violarite form a continuous solid solution at 300°C (Craig, 1971). The composition of the polydymite-ss grains in rocks from Hole 1268A are consistent with a (Fe, Ni)3S4 phase stable at 400°C, but they are too rich in Ni to have formed at 450°C. The polydymite-ss composition of the Hole 1268A samples is consistent with the rather high alteration temperatures of 350°C and higher deduced from oxygen isotope data.

Redox conditions during serpentinization and steatitization

Previous studies revealed that sulfides, oxides and alloys in the Fe–Ni–O–S system are indicative of the redox conditions during serpentinization (e.g. Eckstrand, 1973; Frost, 1985; Alt & Shanks, 1998). Our petrographic investigations reveal that serpentinization of abyssal peridotites from
Fig. 6. Activity–activity diagrams depicting redox phase equilibria in the Fe–Co–O–S system from 150 to 400°C at 50 MPa. Dashed lines are boundaries of magnetite, hematite, pyrrhotite, and pyrite stability fields; continuous lines are boundaries of cobalt, wairauite, Cobaltpentlandite, linnaeite, and cattierite stability fields. Jaipurite is metastable relative to Cobaltpentlandite and linnaeite, and does therefore not project.
Table 3: Opaque phase assemblages and $\delta^{18}$O isotope data* for the studied samples

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| Pentlandite | ++ | + | + |
| Co-pentlandite | +++ | +++ | + | +++ | +++ | +++ | + | + |
| Awaruite | +++ | +++ | +++ | + | ++ | ++ | + | + |
| Heazlewoodite | +++ | + | +++ | + |
| Godlevskite | +++ |
| Millerite | Polydymite-ss |
| Magnetite | +++ | +++ | +++ | +++ | +++ | +++ | +++ | + |
| Pyrite | Chalcopyrite |
| Serpentine | +++ | +++ | +++ | +++ | +++ | +++ | +++ | |
| Brucite | +++ | + | + | + | + | ++ | +++ |
| Talc | + | + | vein |

$\delta^{18}$O isotope data are from Alt et al. (2007).

*+, scarce; ++, abundant; ++++, very abundant; Du, dunite; Hz, harzburgite; mbsf, metres below sea floor.
ODP Leg 209 is accompanied by changing Fe–Ni–Co–O–S phase assemblages. In partly serpentinized peridotites, pentlandite + awaruite + magnetite and pentlandite + heazlewoodite + magnetite are the dominant assemblages. Fe–Ni–O–S minerals in serpentinites from ODP Leg 209 are volumetrically insignificant (<0.1 vol.%) and hence incapable of buffering H$_2$aq. Changes in Fe–Ni–O–S assemblage mineralogy apparently monitor changes in H$_2$aq activity superimposed by reactions between seawater-derived fluids and phases in the MgO–FeO–Fe$_2$O$_3$–SiO$_2$–H$_2$O system.

A reaction commonly observed in thin section is the desulfurization of pentlandite to awaruite and magnetite that is driven by the large quantities of H$_2$aq released during serpentinization:

\[
\text{Ni}_33\text{Fe}_4\text{S}_8 + 6\text{H}_2\text{O} \rightarrow 15\text{Ni}_3\text{Fe} + 15\text{Fe}_3\text{O}_4 + 8\text{H}_2\text{S}_aq
\] (1)

The reaction indicates extremely low oxygen and sulfur fugacities in the system.

Pentlandite + awaruite + magnetite equilibria in the absence of heazlewoodite imply hydrogen concentrations close to or at the solubility of dihydrogen in water, in particular between 200 and 350°C (Fig. 4). Awaruite and heazlewoodite never co-occur in one assemblage, although they may co-occur in the same thin section. The assemblage consisting of pentlandite, heazlewoodite, and magnetite indicates H$_2$aq activities just below dihydrogen saturation of the fluids. This assemblage suggests that pentlandite breakdown is now by the reaction

\[
\text{Ni}_33\text{Fe}_4\text{S}_8 + 6\text{H}_2\text{O} \rightarrow 15\text{Ni}_3\text{Fe} + 15\text{Fe}_3\text{O}_4 + 8\text{H}_2\text{S}_aq
\] (2)

whereas awaruite breaks down by the reaction

\[
3\text{Ni}_3\text{Fe} + 6\text{H}_2\text{S}_aq + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 3\text{Ni}_3\text{S}_2 + 10\text{H}_2\text{aq}.
\] (3)

Both reactions indicate increasing oxygen fugacities; the latter also suggests increasing sulfur fugacities compared with conditions during the breakdown of pentlandite to awaruite. Although there is ample evidence for pentlandite breakdown to heazlewoodite and magnetite in thin section (Fig. 2f), the actual awaruite breakdown reaction is not recorded in a specific assemblage, so it is uncertain if reaction (3) does indeed take place.

At 400°C the awaruite stability field expands into the pyrrhotite field. Here, the assemblage pentlandite + awaruite + magnetite is not stable.

**Redox conditions during steatitization**

The opaque phase assemblages we found in steatized serpentinites are completely different from those found in partly to fully serpentinized peridotites. With increasing degree of steatitization magnetite is replaced by pyrite and sulfur-poor Ni sulfides are progressively replaced by sulfur-rich Ni sulfides. These transitions indicate increasing oxygen and sulfur fugacities (see Eckstrand, 1975; Frost, 1985). During steatitization of serpentinized peridotites millerite grows at the expense of the sulfur-poor Ni sulfides heazlewoodite and godlevskite (Fig. 2j). The direct replacement of pentlandite or awaruite by millerite was not observed, although it may take place if $f_{O_2}$ increases rapidly:

\[
\text{Ni}_3\text{S}_2 + \text{H}_2\text{S}_aq \rightarrow \text{H}_2\text{aq} + 3\text{NiS}
\] (4)

\[
\text{Ni}_9\text{S}_8 + \text{H}_2\text{S}_aq \rightarrow \text{H}_2\text{aq} + 9\text{NiS}.
\] (5)

The replacement of magnetite by pyrite is represented by the reaction

\[
\text{Fe}_3\text{O}_4 + 6\text{H}_2\text{S}_aq \rightarrow 2\text{H}_2\text{aq} + 4\text{H}_2\text{O} + 3\text{FeS}_2.
\] (6)

Reactions (4)–(6) indicate decreasing H$_2$aq and increasing H$_2$S$_aq$ activities. With progressive steatitization the replacement of millerite by polydymite-$ss$ (Fig. 2k), indicates a further decrease in H$_2$aq and an increase in H$_2$S$_aq$ activities:

\[
3\text{NiS} + \text{H}_2\text{S}_aq \rightarrow \text{H}_2\text{aq} + \text{Ni}_3\text{S}_4
\] (7)

\[
6\text{NiS} + \text{Fe}_3\text{O}_4 + 6\text{H}_2\text{S}_aq \rightarrow 2\text{H}_2\text{aq} + 4\text{H}_2\text{O} + 3\text{FeNi}_3\text{S}_1.
\] (8)

In partly steatitized serpentinites magnetite + millerite + pyrite ± polydymite is the dominant assemblage (Fig. 2k). Although this is not an equilibrium assemblage, these phases do represent a small range in H$_2$aq–H$_2$S$_aq$ activities at 350°C (Fig. 4).

The solubility of vaesite in pyrite at temperatures <400°C is below 2 mol %, whereas the maximum solubility of vaesite in pyrite is 7.5 mol % at temperatures around 700°C (Clark & Kullerud, 1963). The high Ni concentrations in pyrite from Hole 1268A (up to 7.44 mol %) in combination with alteration temperatures around 350°C suggest that the solution of Ni in pyrite is metastable. This, in turn, implies that H$_2$aq–H$_2$S$_aq$ activities were in the stability region of vaesite. The Ni-rich pyrite in Hole 1268A hence is the phase representing the highest sulfur fugacities—or lowest $f_{H_2S,aq}$ / highest $f_{H_2S,aq}$ conditions (Figs. 4–6). This type of mineralization appears tightly linked to the formation of talc in veins and steatitization of serpentinite.

In addition to forming vaesite from polydymite in the course of increasing sulfur fugacities,

\[
\text{Ni}_3\text{S}_4 + 3\text{S}_2,g \rightarrow 3\text{NiS}_2
\] (9)
vaesite-rich pyrite along with millerite may replace polymyrite-

\[
\text{Fe}_8\text{Ni}_3\cdots\text{S}_4 \rightarrow \text{Fe}_8\text{Ni}_1\cdots\text{S}_2 + 2\text{NiS. (10)}
\]

Our thermodynamic analyses indicate that this reaction is favorable with decreasing temperatures (Fig. 4).

**Implications for a potential H\(_2\)S,aq buffer in serpentinite-hosted hydrothermal systems**

We next examine if the sulfide assemblages observed in veins (i.e. unit water activities) are consistent with H\(_2\)S,aq concentrations measured in high-temperature vent fluids from ultramafic-hosted hydrothermal systems. Fluids venting at the Rainbow or Logatchev hydrothermal fields have uniform H\(_2\)S concentrations of around 1 mmol/kg (nM) (Charlou et al., 1998, 2002; Schmidt et al., 2007). We can relate the aqueous H\(_2\)S concentrations of interacting fluids with estimated sulfur and oxygen fugacities from phase relations, if we explore the equilibrium of the reaction

\[
\text{S}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{S,aq} + \text{O}_2\text{,g}
\]  

(see Frost, 1985). To determine which phases could be in stable coexistence with a fluid with 1 mM H\(_2\)S at 350°C, we plotted an H\(_2\)S,aq isopotential of 1 mM in Fig. 5. Remarkably, at 350°C and 50 MPa the 1 mM H\(_2\)S,aq isopotential follows the \(f_\text{S}_2 / f_\text{O}_2\) evolution trend revealed by the succession of Fe–Ni–O–S phase relations observed. It can thus be suggested that H\(_2\)S,aq in serpentinite-hosted hydrothermal systems is buffered by equilibria between the Fe–Ni–O–S phases, H\(_2\)S concentrations in the alkaline lower temperature Lost City hydrothermal vent fluids are less well constrained, but exploratory data (Kelley et al., 2001; Dulov et al., 2005) are suggestive of H\(_2\)S activities that are active in the range of several J/mol/kg. Such low H\(_2\)S activities are entirely consistent with buffering by pentlandite breakdown reactions at estimated reaction zone temperatures (Allen & Seyfried, 2004) of 200°C (Fig. 4).

An alternative explanation was provided by Seyfried et al. (2004), who hypothesized that the high H\(_2\)S,aq and low H\(_2\)S,aq concentrations found in these systems suggest magnetite + bornite + chalcoite + fluid equilibria at 400°C and 50 MPa. Although this interpretation is entirely consistent with the thermodynamic data, we have not yet observed the magnetite + bornite + chalcoite assemblage in altered peridotite. Perhaps the serpentinites and soapstones drilled from the area around Logatchev are unlike rocks in the reaction / upflow zones underneath the Logatchev vent field. Our preferred interpretation, however, is that H\(_2\)S,aq is set by pentlandite-desulfurization reactions.

Metal sulfides are trace components in altered peridotite (in particular Cu sulfides), so it appears unlikely that they buffer a major fluid species such as dissolved H\(_2\), except perhaps in a mineralized upflow zone. In a subsequent paper we will show that the levels of dissolved H\(_2\) in the Logatchev and Rainbow hydrothermal fluids are entirely consistent with serpentinization reactions at 400°C. Our preliminary conclusion is that there is no unique H\(_2,aq\)–H\(_2\)S,aq buffer in peridotite-hosted systems, but H\(_2\)S,aq should be set by phase equilibria to values around 1 mM at temperatures around 350–400°C. However, we do not seem to have a sample of a rock that represents a reaction zone of a high-temperature vent fluid. Rocks from Hole 1274A reveal low alteration temperatures, whereas rocks from Hole 1268A have Fe–Ni–O–S phase relations inconsistent with the H\(_2,aq\)–H\(_2\)S,aq systematics of the vent fluids. The problem of whether or not there is a unique H\(_2,aq\)–H\(_2\)S,aq buffer and what that buffer might be requires further examination.

**Sulfur metasomatism**

Total sulfur contents of rocks from ODP Leg 209 range from 0.003 to 2.1 wt % (Paulick et al., 2006; Alt et al., 2007). They are variably depleted or enriched compared with the depleted upper mantle (~0.02 wt %; Salters & Stracke, 2004). As our petrographic observations reveal, main-stage serpentinitization results in desulfurization of primary sulfide (see Alt & Shanks, 1998). Consequently, sulfur should be lost from the rocks during serpentinitization. Indeed, sulfur concentrations in many serpentinite samples are below 0.012 wt % (Fig. 7). In a plot of SiO\(_2\) vs ZS data partly serpentinized peridotites with modal brucite (those with SiO\(_2\) < 10 wt %) have distinctly lower ZS compared with completely serpentinized and steatized rocks. The latter can have sulfur contents of the order of 2 wt %. What is the source of that sulfur and why do sulfides become enriched in the course of steatitization?

Hydrogen produced in copious amounts during serpentinitization will keep sulfur fugacities low and push sulfur out of primary sulfides into dissolved H\(_2\)S:

\[
\text{S}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{S,aq} + \text{O}_2\text{,g}
\]  

(11)

Primary sulfides in fresh peridotite will desulfurize and become obliterated during serpentinitization:

\[
\text{FeS(in primary sulfide) + H}_2\text{,aq} = H_2\text{S,aq} + \text{Fe(in awaruite). (13)}
\]

When serpentinitization nears completion the conditions become less reducing and reaction (13) proceeds to the left, allowing mineralization with high sulfur fugacity assemblages such as observed in Hole 1268A to develop. One possible explanation for the sulfur enrichment in completely serpentinized peridotites is a moving serpentinitization front. Sulfur is leached from the peridotite during active serpentinitization, removed by the serpentinitization front and reprecipitated in rocks where serpentinization is
complete. Perhaps the parts of the system that undergo active serpentinization are regions where percolating fluids pick up H$_2$S,aq that they will subsequently dump in sulfides in areas where increased sulfur and oxygen fugacities prevail. The H$_2$S,aq front, however, would have to be fairly subdued, as even the low sulfur fugacity phases would buffer H$_2$S,aq concentration to values of the order of 1 mM (see above). To create the sulfide accumulations observed in Hole 1268A, one would need to flux a substantial amount of serpentinization fluids through a zone that has externally controlled high sulfur and oxygen fugacities. Such a zone could potentially be the peripheral parts of hydrothermal upflow zones, where upwelling reduced fluids mix with entrained seawater. Not only would the physicochemical changes in those areas of fluid mixing be conducive to sulfide precipitation, but also seawater sulfate would constitute an external source of sulfur, which could be reduced thermogenically by dihydrogen dissolved in the hot upwelling fluids. Indeed, the sulfur isotope composition of hydrothermal sulfide veins from Hole 1268A ($\delta^{34}$S = 5−11‰; Alt et al., 2007) indicates that reduced seawater sulfate is a significant source of sulfur besides sulfide leached from the basement. Similarly, Beard & Hopkinson (2000) found marcasite accumulations associated with a fossil vent in Hole 1068 (Leg 173; Iberian Margin) and concluded that the sulfide was precipitated from seawater interacting with reducing fluids venting from the serpentinite.

It appears that both sulfur- and silica-metasomatism are somehow related. However, some weakly steatized serpentinites have exceedingly high sulfur contents (Fig. 7; see Paulick et al., 2006) indicating that the sulfur-metasomatism preceded the silica-metasomatism. In those samples, steatitization starts in serpentinite veins or where serpentine pseudomorphs pyroxene (bastite). In contrast, serpentine replacing olivine is apparently unaffected by steatitization. Because bastite and vein serpentine are usually devoid of brucite they can be readily transformed into talc, whereas brucite intergrown with serpentine in the mesh-textured groundmass sucks up the silica before serpentine can be transformed into talc. Apparently the introduction of silica to the system leads to increased oxygen and sulfur fugacities that, in turn, promote sulfide precipitation. Aqueous silica plays a role in setting oxygen fugacities, as hydrogen production tied to magnetite formation will be facilitated at low silica activities; for example,

\[
3\text{Fe}_2\text{SiO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2,\text{aq} + \text{H}_2,\text{aq} \quad (14)
\]

or

\[
\text{Fe}_5\text{Si}_2\text{O}_5(\text{OH})_3 \rightarrow \text{Fe}_3\text{O}_4 + \text{SiO}_2,\text{aq} + \text{H}_2\text{O} + \text{H}_2,\text{aq}. \quad (15)
\]

As long as brucite is present, it will keep silica activities low; that is, at the brucite–serpentine buffer, which is 3–4 orders of magnitude below quartz saturation (e.g., Frost & Beard, 2007). As silica activity goes up, reaction (15) may be reversed and Fe-rich serpentine forms. That reaction
would provide a sink for $H_2$ that is required to pyritize magnetite [see reaction (5)].

Because talc does discriminate against Fe much more than serpentine, the sulfide precipitation peaks during silica metasomatism immediately after brucite has reacted out, but before replacement of serpentine by talc is complete. The source of silica is most probably gabbroic intrusions (Bach et al., 2004); such intrusions have also been proposed to explain the sulfur and S isotopes systematics (Alt et al., 2007). Both silica- and sulfur-enrichments in rocks from Hole 1268A can, therefore, be best explained by the involvement of gabbroic lithologies, which are frequently found in Hole 1268A and elsewhere in the 15°20′N Fracture Zone area (see Kelemen et al., 2007).

Possible existence of a free $H_2$-rich vapor phase

As demonstrated above, pentlandite + awaruite + magnetite equilibria imply hydrogen concentrations close to or at the solubility of dihydrogen in water, in particular between 200°C and 350°C (Fig. 5). Because temperature estimates for alteration of rocks from ODP Leg 209 largely overlap with this temperature range, a free $H_2$-rich vapor phase may exist in abyssal serpentinization systems. In continental settings active serpentinization produces $H_2$-rich gas emanations (e.g. Thayer, 1966; Coveney, 1971; Barnes et al., 1978; Yurkova et al., 1982; Coveney et al., 1987; Abrajano et al., 1988; Sturchio et al., 1989). Although the hydrostatic pressure in the deep sea will increase the solubility of dihydrogen, serpentinization of abyssal peridotites may produce a free $H_2$-rich vapor phase. This has been proposed previously, based on experimental work (McCollom & Seewald, 2001, 2006) and theoretical considerations (Sleep et al., 2004). Our calculations provide additional support for the idea that $H_2$ concentrations close to or exceeding hydrogen solubilities may develop during serpentinization. Figure 8 compares the $H_2$ concentrations corresponding to awaruite–pentlandite–magnetite–heazlewoodite equilibria

$$\text{Ni}_4\text{Fe}_{1.5}\text{S}_8 + 9\frac{1}{2}\text{H}_2\text{O} + 2\frac{1}{2}\text{Ni}_3\text{Fe} = 9\frac{1}{2}\text{H}_2\text{aq} + 2\frac{1}{2}\text{Fe}_3\text{O}_4 + 4\text{Ni}_3\text{S}_2$$

with that of equilibrium $H_2g = H_2\text{aq}$. As indicated in the phase diagrams presented above, awaruite-bearing assemblages represent extremely high $H_2\text{aq}$ concentrations close to saturation, in particular in the 200–300°C temperature range. The effect of pressure is also considered in the calculations and illustrated in Fig. 8.

Hydrogen concentrations actually measured in fluids venting from peridotite-hosted hydrothermal systems (e.g. Charlou et al., 2002) are one or two orders of magnitude lower than the maximum values expected. However, Lost City fluid hydrogen concentrations of 15 mM (Proskurowski et al., 2006) are undersaturated at a hydrogen partial pressure of 7.5 MPa (ambient pressure at Lost City) by only a factor of five.

Awaruite has been assigned a critical role in methanogenesis and Fischer–Tropsch-type synthesis of organic compounds in hydrothermal systems (Horita & Berndt, 1999; McCollom & Seewald, 2001). We suggest that the presence of awaruite in a rock indicates that the interacting fluids may have exsolved a $H_2$ gas phase, which would also make a very efficient catalyst for organic synthesis reactions (McCollom & Seewald, 2006). Whether or not a hydrogen-rich gas phase forms during serpentinization depends on the pressure (Fig. 8). Our calculation results suggest that a free hydrogen gas phase could potentially develop at pressures <50 MPa.

$H_2$- and $CH_4$-rich fluid inclusions observed in deep-seated gabbroic rocks from the ocean crust (e.g. Kelley, 1997; Kelley & Früh-Green, 2001) may provide evidence for the development of fluid exsolution. Further examination of this hypothesis will rely on improved estimates of the pressure–temperature conditions of peridotite–fluid interaction.

CONCLUSIONS

We propose that Fe–Ni–Co–O–S phase relations provide a very useful monitor for the evolution of temperature and the fugacities of sulfur and oxygen during peridotite–seawater interaction. Our results demonstrate that peridotites...
from Hole 1274A were serpentinized at uniformly reducing conditions and relatively low temperatures of <300°C. Steatitization superimposed on serpentinization resulted in increasing oxygen and sulfur fugacities.

Sulfur-metasomatism affecting fully serpentinized peridotites is related to steatitization. The evolution of SiO$_2$, H$_2$ and H$_2$S activities is coupled. Dihydrogen drops when brucite is exhausted by reaction with high-$\alpha$SiO$_2$ fluids probably derived from interactions with gabbroic bodies that make up a large fraction of the lithosphere in the 15°20’N Fracture Zone area. As H$_2$aq activity drops, high-sulfur-fugacity phases such as pyrite and polylithnite precipitate. The sequence of events leads to early pervasive sulfide leaching followed by late and localized sulfur enrichment.

Associated with the prominent desulfurization of pentlandite, sulfide is removed from the rock during the initial stage of serpentization. In contrast, steatitization indicates increased silica activities, and high-sulfur-fugacity sulfides, such as polylithnite and pyrite–vaesite solid solution, form as the reducing capacity of the peridotite is exhausted and H$_2$ activities drop. Under these conditions, sulfides will not desulfurize but precipitate, leading to an enrichment of S, as seen in rocks from Site 1268.

The co-evolution of $\Delta$O$_2$/$\Delta$S$_2$ in the system follows an isopotential of H$_2$S,aq, indicating that H$_2$Si environs are coupled. Dihydrogen drops when brucite is exhausted by reaction with high-$\alpha$SiO$_2$ fluids probably derived from interactions with gabbroic bodies that make up a large fraction of the lithosphere in the 15°20’N Fracture Zone area. As H$_2$aq activity drops, high-sulfur-fugacity phases such as pyrite and polylithnite precipitate. The sequence of events leads to early pervasive sulfide leaching followed by late and localized sulfur enrichment.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available at Journal of Petrology online.

REFERENCES


Klein and Bach Peridotite–Seawater Interactions


