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2. Data Report: Microprobe Analyses of Primary Phases (Olivine, Pyroxene, and Spinel) and Alteration Products (Serpentine, Iowaite, Talc, Magnetite, and Sulfides) in Holes 1268A, 1272A, and 1274A[1]

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INTRODUCTION

Primary and secondary mineral phases from Holes 1268A (11 samples), 1272A (9 samples), and 1274A (12 samples) were analyzed by electron microprobe in Bonn and Cologne (Germany) (Table T1). Bulk rock powders of these samples were also analyzed geochemically, including major and trace elements (Paulick et al., 2006).

Ocean Drilling Program (ODP) Leg 209 Holes 1268A, 1272A, and 1274A differ remarkably in alteration intensity and mineralogy, and details regarding their lithologic characteristics are presented in Bach et al. (2004) and Shipboard Scientific Party (2004).

Hole 1274A contains the least altered peridotite drilled during Leg 209; however, the abundance of serpentine-brucite-magnetite assemblages increases from 60 to >95 vol% downhole. In Hole 1272A, completely serpentinized harzburgite consists of serpentine-magnetite ± brucite ± iowaite assemblages. Iowaite ($Mg_4[OH]_8Fe^{3+}OCl \cdot 1–4[H_2O]$) has been described previously from submarine mud volcanoes (Heling and Schwarz, 1992) and serpentinites at the Iberian margin (Gibson et al., 1996). Hole 1272A represents the first documented occurrence of this mineral as a replacive phase in a mid-ocean-ridge setting (Shipboard

T1. Mineral analyses, p. 10.

[1]Moll, M., Paulick, H., Suhr, G., and Bach, W., 2007. Data report: microprobe analyses of primary phases (olivine, pyroxene, and spinel) and alteration products (serpentine, iowaite, talc, magnetite, and sulfides) in Holes 1268A, 1272A, and 1274A. *In* Kelemen, P.B., Kikawa, E., and Miller, D.J. (Eds.), *Proc. ODP, Sci. Results,* 209: College Station, TX (Ocean Drilling Program), 1–13. doi:10.2973/odp.proc.sr.209.003.2007
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Scientific Party, 2004), although iowaite has been reported as vein mineral in serpentinite from Hess Deep (Früh-Green et al., 2004).

Hole 1268A contains serpentinized and talc-altered harzburgite and dunite, and serpentinites contain as much as 3 vol% pyrite and other sulfide minerals, which are otherwise rare in the altered peridotite drilled during Leg 209. Talc alteration of serpentinites under static conditions is interpreted to be the result of Si metasomatism (Bach et al., 2004; Shipboard Scientific Party, 2004).

Because of the least altered character of peridotite in Hole 1274A, abundant clinopyroxene, orthopyroxene, olivine, and spinel were analyzed at this site. In Hole 1272A, primary silicates are rare and analyses were restricted to some samples that contain traces of olivine and orthopyroxene. Because of the intensity of alteration, Hole 1268A is devoid of primary phases except spinel. Commonly, alteration is pseudomorphic and serpentinization of olivine and orthopyroxene can be distinguished. Accordingly, compositional variations of the alteration minerals with regard to the precursor minerals are one of the issues investigated in this data report.

METHODS

The analyses were obtained at the microprobe laboratories at Bonn and Cologne Universities (Germany) (Tables T2, T3, T4). At Bonn, 536 individual analyses were performed using a Cameca Camebax Microbeam under operating conditions of 15 kV and 15 nA beam current and a beam diameter of 1.5–2 µm. Counting times were 40 s for Cl (detection limit = 0.01 wt%) and 20 s for all other elements analyzed (Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn). Data were corrected using the ZAF correction (Z = atomic number, A = adsorption, and F = fluorescence) from Pouchou and Pichoir (1984).

T2. Microprobe analyses, Hole 1274A, p. 11.

T3. Microprobe analyses, Hole 1272A, p. 12.

T4. Microprobe analyses, Hole 1268A, p. 13.

A JOEL EMP8900 microprobe was used for 364 individual analyses at Cologne. The operating conditions for olivines were 20 kV and 50 nA. All other minerals were analyzed applying 15 kV and 20 nA (beam diameter focused to ~1.5–2 µm). Counting times were 10 s for Na and K, 50 s for Ti, 50 s for Ni in olivine, and 20 s for the other elements. The ZAF data correction was also applied.

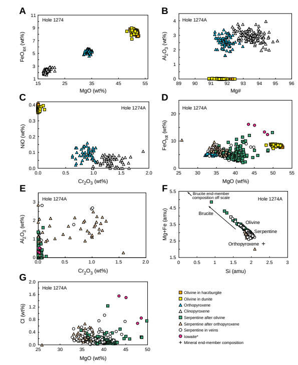
The standards used in Bonn were jadeite-diopside$_{SS}$ (Na, Ca, and Si), sanidine (K), corundum (Al), periclase (Mg), rutile (Ti), apatite (Cl), sphalerite (Zn), and elemental Fe, Cr, Mn, Ni, and Cu. In Cologne, diopside (Mg, Ca, and Si), Cr_2O_3 (Cr), NiO (Ni), FeO (Fe), corundum (Al), orthoclase (K), albite (Na), rutile (Ti), and rhodonite (Mn) were employed as standard materials. The mineral formulas calculated are based on the following oxygen bases: olivine, 4; pyroxene, 6; spinel, 4; serpentine, 7; talc, 22; and iowaite, 5. The sulfides analyses were recalculated based on four cations.

Hole 1274A

Many samples show a comparatively low degree of alteration (<80 vol% alteration minerals), and variable proportions of orthopyroxene, clinopyroxene, olivine, and spinel are present in samples of altered harzburgite and dunite. Orthopyroxene and olivine are altered to serpentine, and brucite (after olivine) is locally present. Brucite was also detected in Hole 1274A by shipboard X-ray diffraction (XRD) measurements (Shipboard Scientific Party, 2004).

Clinopyroxene compositions were determined in 12 samples and compositional variation is limited (average = $En_{51}Fs_3Wo_{45}$). The clinopyroxenes are diopsides with low FeO (1.7–2.9 wt%) and a limited range in MgO (17.0–21.3 wt%) (Fig. **F1A**) content and Mg# (92.3–95.1) (Fig. **F1B**). Orthopyroxenes are enstatitic in composition with somewhat higher contents of FeO (4.6–5.8 wt%) (Fig. **F1A**) and lower Mg# (91.2–93.0) (Fig. **F1B**) than clinopyroxene. The olivines are forsterite rich with 7.3–9.0 wt% FeO and 48.2–52.5 wt% MgO (Fig. **F1A**). Olivines in harzburgites tend to lower FeO contents and higher Mg# than olivines in dunite (Fig. **F1A, F1B**). In Figure **F1C,** NiO from olivines, orthopyroxenes, and clinopyroxenes is plotted against Cr_2O_3. NiO contents in olivines range between 0.35 and 0.41 wt% and correlate with low Cr_2O_3 content (up to 0.12 wt%). In contrast, orthopyroxenes and clinopyroxenes show higher Cr_2O_3 (0.6–1.9 wt%) and lower NiO (up to 0.16 wt%) contents.

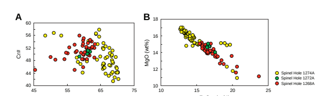
F1. Variations of primary and secondary phases, Hole 1274A, p. 6.



Serpentines show considerable compositional range, which is in part related to variability in precursor mineral composition. In general, serpentine pseudomorphs after orthopyroxene have lower MgO contents (25.8–38.3 wt%) than serpentines formed after olivine (MgO = 34.8–49.8 wt%); however, some overlap is apparent (Fig. **F1D**). In a similar fashion, most of the serpentine formed after orthopyroxene has considerably higher Al_2O_3 and Cr_2O_3 concentrations than serpentine formed after olivine (Fig. **F1E**). However, many of the analyses of serpentine replacing olivine have higher Mg contents than what could be accommodated in the serpentine mineral structure (Fig. **F1F**). These are most likely mixed analyses of finely intergrown serpentine and brucite formed during hydration reactions of olivine under low a_{SiO2} conditions (Bach et al., 2006). In a similar fashion, some serpentine analyses with particularly elevated Cl concentrations (0.7–1.6 wt%) (Fig. **F1G**) could be attributable to finely intergrown iowaite.

Analyses of magnetite show that magnetites are close to the end-member composition (FeO_{tot} = 76.6–93.3 wt%). The spinels show a negative correlation of Cr# (41.4–57.8) and Mg# (48.5–70.3) (Fig. **F2A**). Variations in FeO_{tot} (12.7–20.7 wt%) and MgO (10.9–17.0 wt%) concentrations are correlated (Fig. **F2B**).

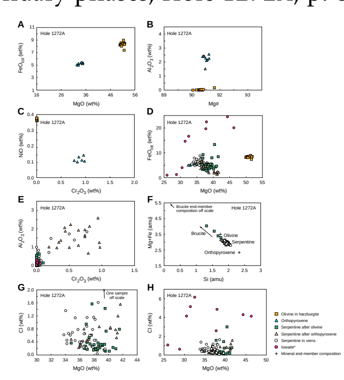
F2. Cr# vs. Mg# and MgO vs. FeO_{tot}, p. 7.



Hole 1272A

Serpentinization is generally complete in Hole 1272A; however, relics of olivine and orthopyroxene could be analyzed in six samples. A total of 21 analyses of olivine and 9 of orthopyroxene show similar compositional characteristics to olivine and orthopyroxene in Hole 1274A. Enstatitic orthopyroxene (En_{86} to En_{90}) contains ~5 wt% FeO and 1.5–2.6 wt% Al_2O_3, and the forsteritic olivine (Mg# = 91–93) contains 0.36–0.4 wt% NiO (Fig. **F3A, F3B, F3C**).

F3. Variations of primary and secondary phases, Hole 1272A, p. 8.



The serpentines pseudomorphing orthopyroxene and serpentine after olivine are similar in MgO and FeO contents (Fig. **F3D**). Only a few analyses of serpentine after olivine with elevated Mg + Fe contents could be interpreted as an indication of intergrown brucite (Fig. **F3F**). However, there are systematic differences in Cr and Al contents (Fig. **F3D, F3E**). Serpentine formed after orthopyroxene has considerably higher Al_2O_3 and Cr_2O_3 concentrations than serpentine formed after olivine.

The serpentinites of Hole 1272A are notable for the occurrence of the Cl-rich mineral iowaite (Shipboard Scientific Party, 2004). The presence of iowaite is reflected in the high Cl content of serpentine analyses, ranging mainly from 0.2 to 3.0 wt% (Fig. F3G), whereas the Cl content in serpentines from Hole 1274A, ranges between 0.01 and 1.24 wt% (Fig. F1G). The iowaite mix analyses show wide variations in Cl (0.6–6.2 wt%) and MgO (26–46.3 wt%) contents (Fig. F3H).

The few measured spinels are Cr rich (41.3–42.9 wt%) and correlate in FeO_{tot} and MgO contents (Fig. F2B).

Hole 1268A

Peridotite in Hole 1268A is completely altered, including serpentinite and static talc alteration following serpentinization (Bach et al., 2004). Here, fresh pyroxene or olivine are absent and the only primary mineral is spinel.

Serpentine is often intimately associated with talc so that some analyses represent mixtures of these two compositions. However, differences in SiO_2 content clearly separate the bulk of the data (Fig. F4A). Serpentines formed after orthopyroxene generally contain higher concentrations of FeO_{tot}, Al_2O_3, and Cr_2O_3 and lower concentrations of MgO than serpentine formed after olivine (Fig. F4B, F4C). However, these differences, related to the primary precursor mineral, are apparently obliterated during talc alteration (Fig. F4B, F4C).

Consistent with results from XRD analyses (Shipboard Scientific Party, 2004), the microprobe data provide no indication for the presence of brucite in the serpentinites of Hole 1268A (Fig. F4D). This lack of brucite is consistent with the interpretation that serpentinization reached a mature stage in Hole 1268A (Bach et al., 2004). The serpentines show comparatively low chlorine contents (generally well below 0.4 wt%) (Fig. F4E) compared to serpentine analyses of Holes 1272A and 1274A. Talc is also poor in chlorine (<0.05 wt%), and most analyses are close to or below the detection limit.

Spinel is the only primary mineral in Hole 1268A and it has a chromitic composition. Overall, the data occupy the FeO_{tot} and Cr_2O_3-rich end of the compositional spectrum compared to the spinel in Hole 1274A, but they show a positive correlation and lower Cr# (44.9–55.8) and Mg# (45.4–63.4) than found in Hole 1274A (Fig. F2A). The analyzed magnetites show near end-member compositions with high FeO (88.6–91.6 wt%) and low Al_2O_3 (up to 0.21 wt%) contents.

Sulfide minerals were analyzed in 11 samples of Hole 1268A, and the data show that pyrite and pentlandite dominate. The pyrites have Fe as the single cation and an Fe/S ratio of ~0.5. The pentlandite shows high Ni contents and a (Ni + Fe)/S ratio of ~1 (Fig. F4F, F4G). In one sample (209-1268A-3R-1, 29–38 cm) a chalcopyrite crystal was analyzed that contains about equal proportions of Cu and Fe.

F4. Variations of secondary phases, p. 9.

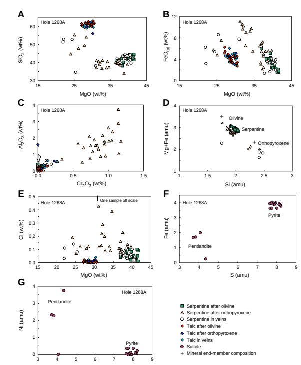


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Figure F1. Plots of chemical variations of primary phases (clinopyroxene, orthopyroxene, and olivine) and secondary phases (serpentine and iowaite) in Hole 1274A. **A.** FeO vs. MgO of primary phases clinopyroxene, orthopyroxene, and olivine. **B.** Al_2O_3 vs. Mg# of primary phases clinopyroxene, orthopyroxene, and olivine. **C.** NiO vs. Cr_2O_3 in orthopyroxene, clinopyroxene and olivine. **D.** FeO_{tot} vs. MgO of primary phases orthopyroxene and olivine and serpentine forming pseudomorphs after olivine and orthopyroxene, filling veins, and iowaite. **E.** Al_2O_3 vs. Cr_2O_3 of serpentine after olivine and orthopyroxene, filling veins, and iowaite. **F.** Cation proportions Mg + Fe vs. Si of serpentine forming pseudomorphs after olivine and orthopyroxene, filling veins, and iowaite (for the figure iowaite is based on 7 O). Mineral end-member compositions are shown (amu = atomic mass units). **G.** Cl vs. MgO of serpentine after olivine and orthopyroxene, filling veins, and iowaite. * = analyses are iowaite-serpentine mixtures.

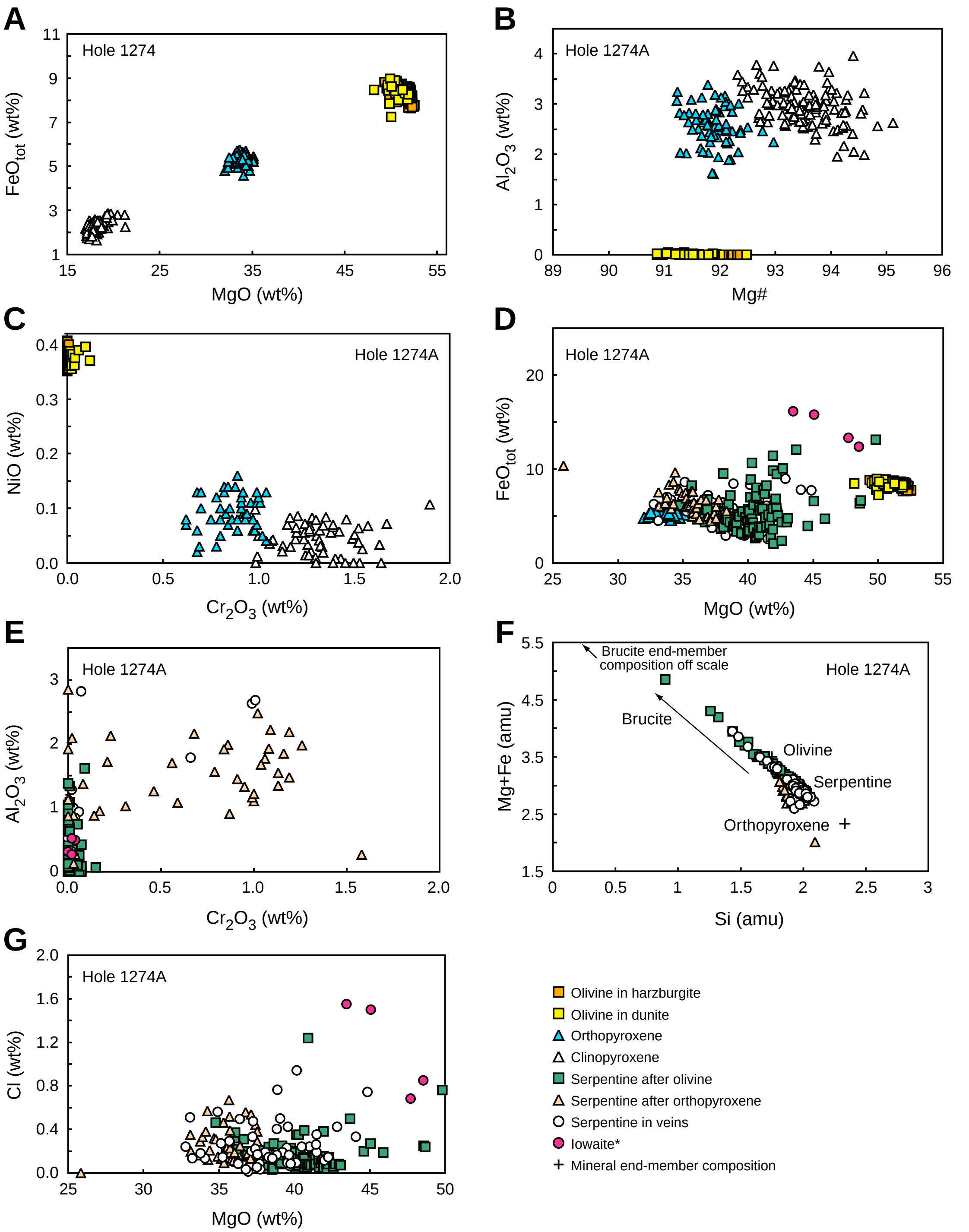

Figure F2. **A.** Cr# vs. Mg# of spinel from Holes 1274A, 1272A, and 1268A. **B.** MgO vs. FeO_{tot} of spinel from Holes 1274A, 1272A, and 1268A.

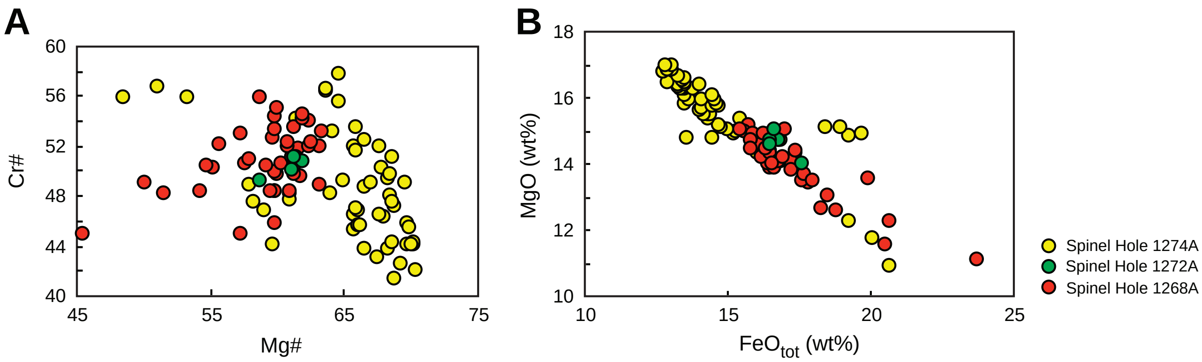

Figure F3. Plots of chemical variations of primary phases (orthopyroxene and olivine) and secondary phases (serpentine and iowaite) in Hole 1272A. **A.** FeO vs. MgO of primary phases orthopyroxene and olivine. **B.** Al_2O_3 vs. Mg# of primary phases orthopyroxene and olivine. **C.** NiO vs. Cr_2O_3 in orthopyroxene and olivine. **D.** FeO_{tot} vs. MgO of primary phases orthopyroxene and olivine and serpentine forming pseudomorphs after olivine and orthopyroxene, filling veins, and iowaite. **E.** Al_2O_3 vs. Cr_2O_3 of serpentine after olivine and orthopyroxene, filling veins, and iowaite. **F.** Cation proportions Mg + Fe vs. Si of serpentine forming pseudomorphs after olivine and orthopyroxene, filling veins, and iowaite (for the figure iowaite is based on 7 O). Mineral end-members are shown (amu = atomic mass unit). **G.** Cl vs. MgO of serpentine after olivine and orthopyroxene, filling veins. **H.** Cl vs. MgO of serpentine after olivine and orthopyroxene, filling veins, and iowaite. * = analyses are iowaite-serpentine mixed analyses.

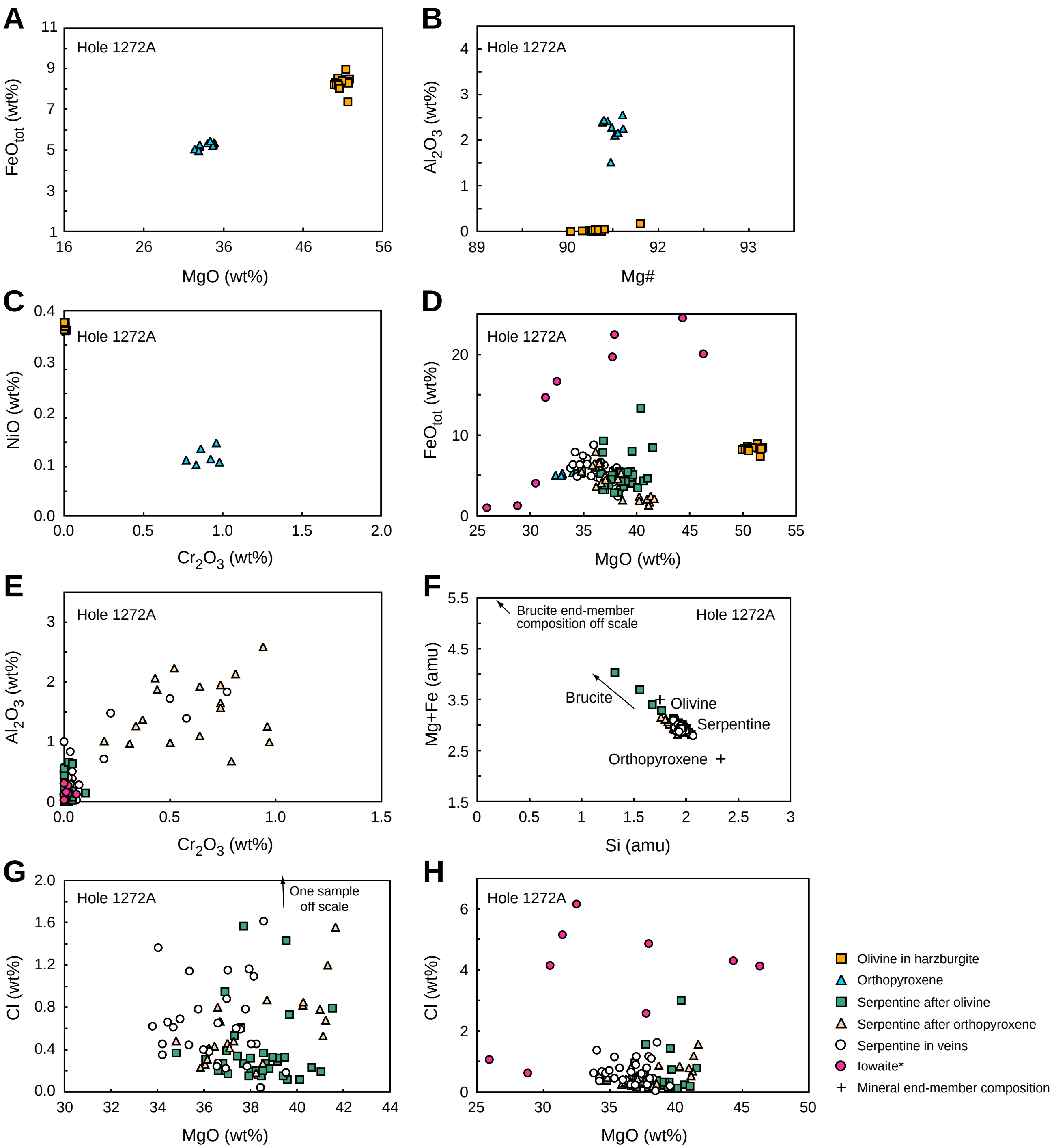

Figure F4. Plots of chemical variations of secondary phases (serpentine, talc, and sulfide) in Hole 1268A. **A.** SiO_2 vs. MgO of serpentine and talc after olivine and orthopyroxene, and filling veins. **B.** FeO vs. MgO of serpentine and talc forming pseudomorphs after olivine and orthopyroxene, and filling veins. **C.** Al_2O_3 vs. Cr_2O_3 of serpentine and talc after olivine and orthopyroxene, and filling veins. **D.** Cl vs. MgO of serpentine and talc after olivine and orthopyroxene, and filling veins. **E.** Cation proportions Mg + Fe vs. Si of serpentine and talc forming pseudomorphs after olivine and orthopyroxene, and filling veins. Mineral end-members are shown (amu = atomic mass unit). **F.** Cation proportions Fe vs. S of sulfides (pentlandite and pyrite). **G.** Cation proportions Ni vs. S of sulfides (pentlandite and pyrite).

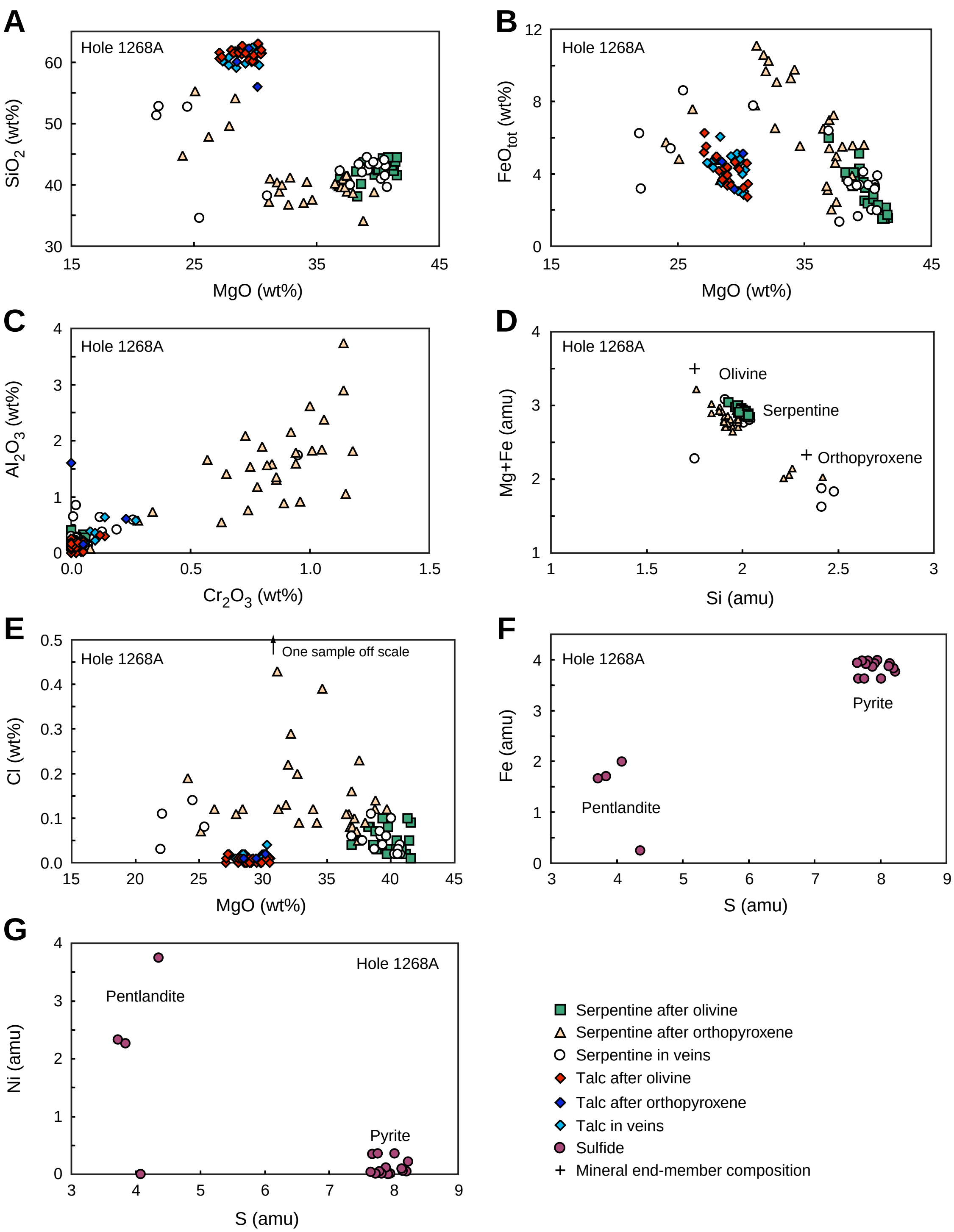

Table T1. Numbers of samples and mineral analyses, Holes 1274A, 1272A, and 1268A.

Hole	Number of samples	Number of analyses											Total
		Olivine	Orthopyroxene	Clinopyroxene	Spinel	Magnetite	Serpentine	Talc	Iowaite	Pyrite	Pentlandite	Chalcopyrite	
209-													
1268A	11	0	0	0	40	4	71	42	0	15	3	1	176
1272A	9	18	9	0	5	0	88	0	9	0	0	0	129
1274A	12	156	65	120	54	6	190	0	4	0	0	0	595
	Total:	174	74	120	99	10	349	42	13	15	3	1	900

Table T2. Microprobe analyses of primary and secondary phases in altered peridotite, Hole 1274A. (This table is available in an **oversized format.**)

Table T3. Microprobe analyses of primary and secondary phases in altered peridotite, Hole 1272A. (This table is available in an **oversized format.**)

Table T4. Microprobe analyses of primary and secondary phases in altered peridotite, Hole 1268A. (This table is available in an **oversized format.**)