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2. Occurrence and Composition of Tochilinite and Related Minerals in Site 1068 Serpentinites[1]

James S. Beard[2]

ABSTRACT

Tochilinite (approximately $FeS \cdot (Mg,Fe)(OH)_2$) is locally abundant in Hole 1068A serpentinites from Cores 173-1068A-21R and 22R. It occurs in veins, as fillings in void space, and in intergrowths with serpentine and andradite. An apparently related mineral, but with Ca and Al largely replacing Mg, occurs in association with, and possibly as a replacement of, pyrrhotite in serpentinite breccias from the bottom of Core 173-1068A-20R. The transition from Mg-Fe–rich brucite tochilinites to Ca- and S-rich carbonate tochilinites is consistent with increasing sulfur and oxygen activity upsection. Tochilinite has been reported at other sites on the Iberia Abyssal Plain and is abundant to the point of being a rock-forming mineral in several samples from Site 1068. Rather than being a mineralogical curiosity, tochilinite appears to be common and a major sink for sulfur in the upper serpentinites of the Iberia Abyssal Plain.

INTRODUCTION

Tochilinite and valleriite are members of a poorly known group of mixed sulfide-hydroxide-(carbonate) minerals, termed here the tochilinite-valleriite group (TVG). TVG minerals have the approximate formula $2(Fe,Ni,Cu)S \cdot N(Mg,Fe,Al,Ca)(OH,CO_3)_{1-2}$, where N is usually between 1 and 2. For purposes of this report, the first part of the formula is referred to as the sulfide component. The second part, which may contain hydroxide, carbonate, and possibly other anions, is re-

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[2]Virginia Museum of Natural History, 1001 Douglas Avenue, Martinsville VA 24112, USA. **jbeard@vmnh.org**

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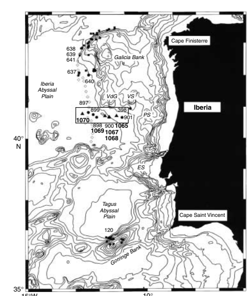
ferred to as the oxide component. The sulfide-oxide ratio; the Cu, Fe, and Ni content of the sulfide component; the Mg, Fe, Ca, and Al content of the oxide component; and the concentration of carbonate in TVG minerals all vary substantially (e.g., Harris and Vaughan, 1972). The extent of compositional variation and solid solution among TVG minerals is poorly known. Valleriite, haapalite, and tochilinite are, respectively, the Cu-, Ni-, and Fe-sulfide–rich members of the TVG. Valleriite is a relatively common secondary phase in copper deposits. Tochilinite occurs in weathered and/or hydrothermally altered mafic and ultramafic rocks, especially serpentinites (Butt and Nickel, 1981; van de Vusse and Powell, 1983; Matsubara and Kato, 1992; Alt and Shanks, 1998). Haapalite is rare.

All three phases occur in the Hole 1068A serpentinites. Valleriite and haapalite are uncommon. Tochilinite, however, is common and probably the dominant sulfur-bearing phase in the upper serpentinites (Cores 173-1068A-21R through 22R).

GEOLOGIC SETTING AND OCCURRENCE OF TVG MINERALS AT HOLE 1068A

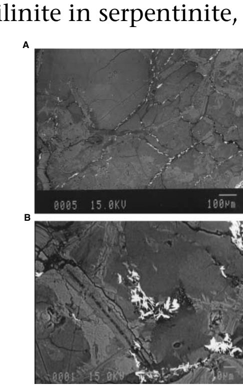
Hole 1068A penetrated a faulted basement high on the Iberia Abyssal Plain (Fig. F1). Basement consists of heterolithic breccias underlain by (and probably in fault contact with) serpentinite (Whitmarsh, Beslier, Wallace, et al., 1998). The Hole 1068A serpentinites are the most landward known occurrence of the serpentinites that directly underlie much of the pelagic sediment in the Iberia Abyssal Plain. These serpentinites appear to represent mantle exposed over an area of tens of thousands of square kilometers during avolcanic rifting (Whitmarsh, Beslier, Wallace, et al., 1998). At Site 1068, both breccias and serpentinite were affected by a hydrothermal system where strongly reducing fluids generated during serpentinization reactions at depth mixed upsection with an oxidized fluid whose composition approximated seawater (Whitmarsh, Beslier, Wallace, et al., 1998; Beard and Hopkinson, 2000). The tochilinite in Hole 1068A occurs near and at the top of the serpentinite, apparently in the zone where the fluids mixed (Whitmarsh, Beslier, Wallace, et al., 1998; Beard and Hopkinson, 2000).

F1. Bathymetric chart of the west Iberia margin, p. 6



Tochilinite was initially identified by shipboard X-ray diffraction measurements on serpentinite from Cores 173-1068A-21R and 22R (Whitmarsh, Beslier, Wallace, et al., 1998). The prominence of the tochilinite peaks in several of these samples suggests that it is an abundant mineral (Whitmarsh, Beslier, Wallace, et al., 1998). Subsequently, tochilinite was identified petrographically in three samples from Cores 173-1068A-20R and 21R. The Core 21R samples are very friable serpentinites containing pentlandite, andradite, and chlorite. In the two samples from Core 21R, tochilinite is abundant, locally constituting several percent of the rock. It occurs in bladelike or sheaflike aggregates (blades <0.01–0.04 mm), mostly in veins or void space (Fig. F2) or as intergrowths with andradite or serpentine. It is opaque in transmitted light. In reflected light, it is pleochroic from reddish yellow to grayish yellow and strongly anisotropic. In hardness and overall form, it resembles graphite. Trace amounts of valleriite were found in two samples (Sample 173-1068A-24R-1 [Piece 5, 34 cm] and 26R-1 [Piece 3D, 49 cm]). It occurs in association with pentlandite, probably as a late reaction or replacement. Haapalite occurs as reaction rims on pentlandite in one

F2. BSE photomicrographs of tochilinite in serpentinite, p. 7.



Core 21R sample (Sample 173-1068A-21R-2 [Piece 1, 110 cm]). In a single sample from serpentinite in Core 20R (Sample 173-1068A-20R-6 [Piece 12, 89 cm]), a Ca- and Al-rich tochilinite occurs as irregular blades and plates that appear to replace pyrrhotite. This mineral is similar to the type I mineral described by Harris and Vaughan (1972). Most of the valleriite reported by Alt and Shanks (1998) from serpentinites elsewhere on the Iberia Abyssal Plain is Fe rich and compositionally similar to the tochilinite at Hole 1068A (J.C. Alt, pers. comm., 1999). Sulfide/metal phases occurring with Iberia Abyssal Plain tochilinites include millerite, godlevskite, pyrrhotite, and native copper (Alt and Shanks, 1998; Whitmarsh, Beslier, Wallace, et al., 1998; Beard and Hopkinson, 2000).

METHODS

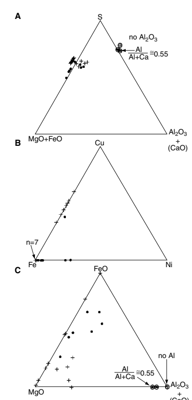
The TVG minerals from Hole 1068A were analyzed on the Cameca SX-50 electron microprobe in the Department of Geologic Sciences at Virginia Polytechnic Institute and State University in Blacksburg, Virginia.

COMPOSITION OF TVG MINERALS

Relatively little compositional data is available for TVG minerals. Comparison of analyses of the Hole 1068A TVG minerals (Table T1) with published analyses (Harris and Vaughan, 1972; Matsubara and Kato, 1992) reveals some of the complexities of TVG chemistry (Fig. F3). Note that most analyses did not report CaO, so, except as noted, variation on Figures F3A and F3C reflects the Mg-Fe-Al ternary. Generally, the sulfide component of TVG minerals is greater than the oxide component. However, several TVG minerals from Hole 1068A have sulfide < oxide. As a group, the (Mg,Fe)-rich tochilinites from Hole 1068A are the most S-poor reported to date (Table T1; Fig. F3A). The highest sulfur concentrations occur in Ca-Al–rich tochilinites from Core 173-1068A-20R and Ca-rich type I tochilinite material from Cyprus (Harris and Vaughan, 1972) (Fig. F3A). Most Hole 1068A TVG minerals are tochilinite, with >90% troilite in the sulfide component. Valleriite and haapalite from Hole 1068A contain, respectively, 40% Cu and 25% Ni in the sulfide component. Published valleriite analyses contain up to 60% of the CuS end-member (Fig. F3B). For the oxide component, nearly pure Mg, Ca, and Fe end-members have all been reported (Fig. F3C). Core 173-1068A-21R tochilinite contains substantial iron in its oxide component. Substantial Al substitution is seen in many TVG minerals from Hole 1068A and elsewhere.

T1. Analyses of tochilinite and related minerals, p. 9.

F3. Compositions of TVG minerals, p. 8.



OCCURRENCE OF TOCHILINITE BENEATH THE IBERIA ABYSSAL PLAIN

Most tochilinite in serpentinites is reported from rocks that, although not deeply weathered themselves, lie immediately below weathered horizons. These include both subaerial and submarine occurrences (van de Vusse and Powell, 1983; Alt and Shanks, 1998). At Holes 1068A, 897C, and 897D on the Iberia Abyssal Plain (Fig. F1), tochilinite is common in serpentinites that occur in a zone beneath rocks containing calcite with pyrite and/or marcasite and above rocks containing more reduced, S-poor minerals (e.g. awaruite) (Alt and Shanks, 1998; Beard and Hopkinson, 2000). This zone appears to be at least 20 m thick at Site 1068 (i.e. comprising Cores 173-1068A-21R and 22R). At Site 1068, tochilinite is interpreted as reflecting a transition in fluid chemistry from reduced, S-poor fluids in the lower serpentinites to more oxidized, S-rich, (seawater-dominated?) fluids closer to the surface (see Beard and Hopkinson, 2000). The change in tochilinite chemistry, from S-poor brucite varieties at depth to S-rich carbonate varieties upsection is consistent with this interpretation.

CONCLUSIONS

The key finding of this report is that tochilinite, rather than being a mineralogical curiosity, is exceptionally abundant at several sites on the Iberia Abyssal Plain. This is especially true in Hole 1068A, where tochilinite achieves the status of a rock-forming mineral over a drilling interval of at least 20 m. As such, it appears to be a major sink for S in the upper portions of many Iberia Abyssal Plain serpentinites and will be important in evaluating S budgets during serpentinization of the vast exposures of peridotite beneath the Iberia Abyssal Plain (e.g., Alt and Shanks, 1998).

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Figure F1. Bathymetric chart of the west Iberia margin. Sites drilled during Leg 173 are shown as solid triangles; other ODP-DSDP sites are shown as solid circles. At this scale, Sites 900, 1067 and 1068 overlap. Sites where samples were collected by dredge or submersible are shown as solid squares. Open diamonds trace the location of the peridotite ridge. Galacia Bank is underlain by continental crust. VdG = Vasco da Gama Seamount, VS = Vigo Seamount, PS = Porto Seamount, and ES = Estremadura Spur. Modified after Whitmarsh, Beslier, Wallace, et al. (1998).

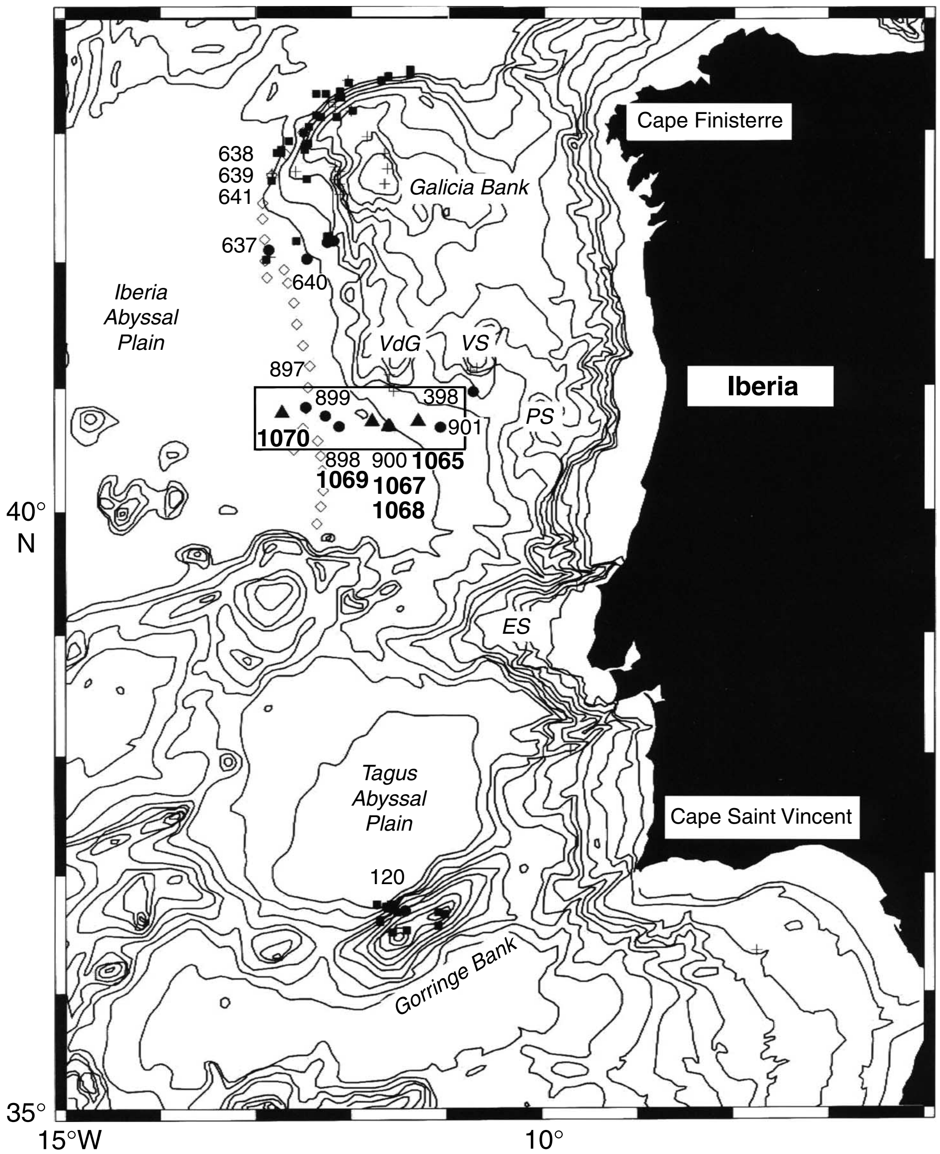

Figure F2. BSE photomicrographs of tochilinite (the bright material in the BSE images) in serpentinite (Core 173-1068A-21R-2, [Piece 1, 110 cm]). **A.** Tochilinite in veins. **B.** Sheaflike aggregates of tochilinite in open veins and voids.

A

B

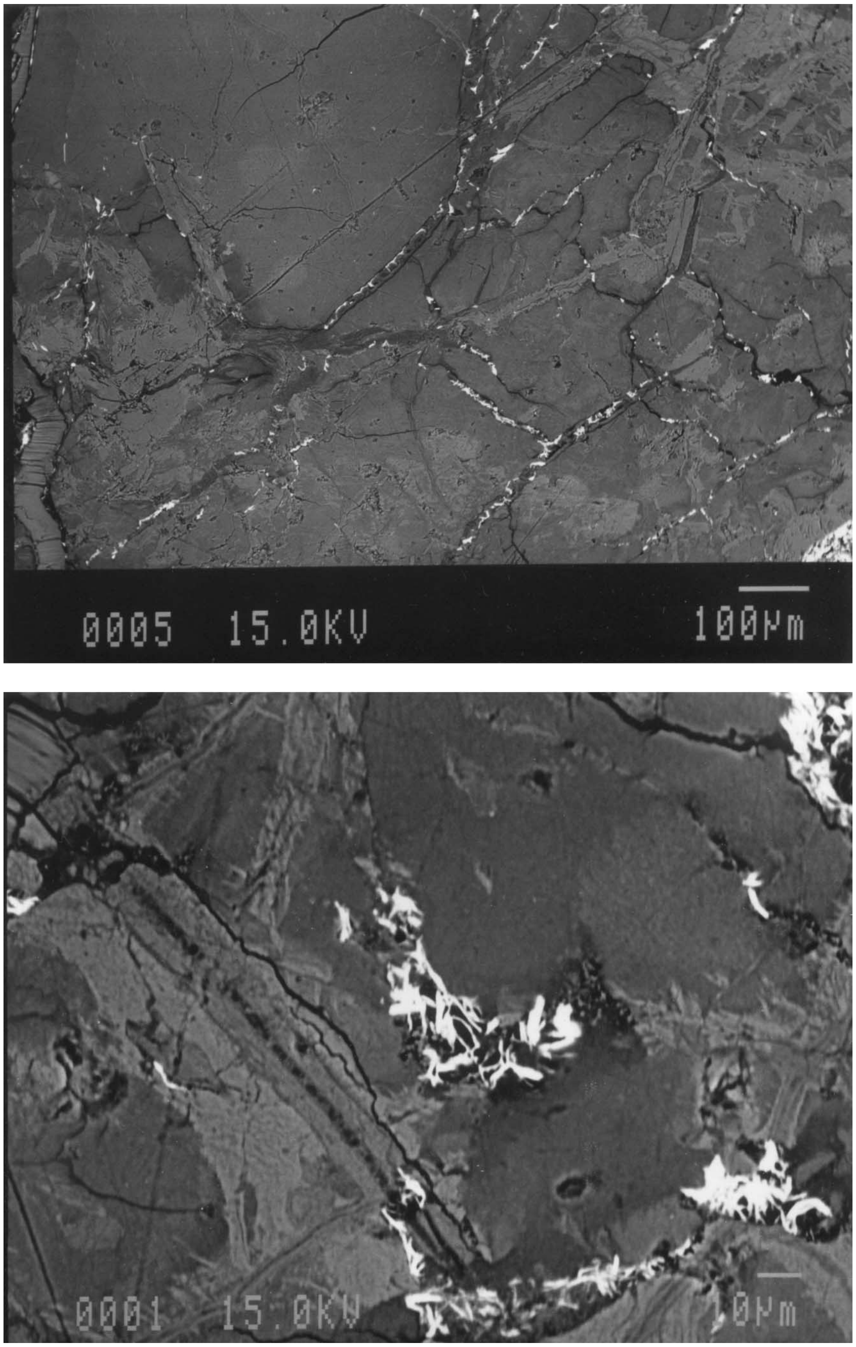

Figure F3. Compositions (mol.) of TVG minerals. **A.** (MgO + FeO) – (Al_2O_3 + CaO)-sulfide, showing sulfide-oxide ratio variability. **B.** Composition of the sulfide component. **C.** Composition of the oxide component. Crosses = literature values given in Matsubara and Kato (1992) and Harris and Vaughan (1972). Solid circles = this report. Circled values include CaO (Al content indicated on figure); all other points include Al_2O_3 only.

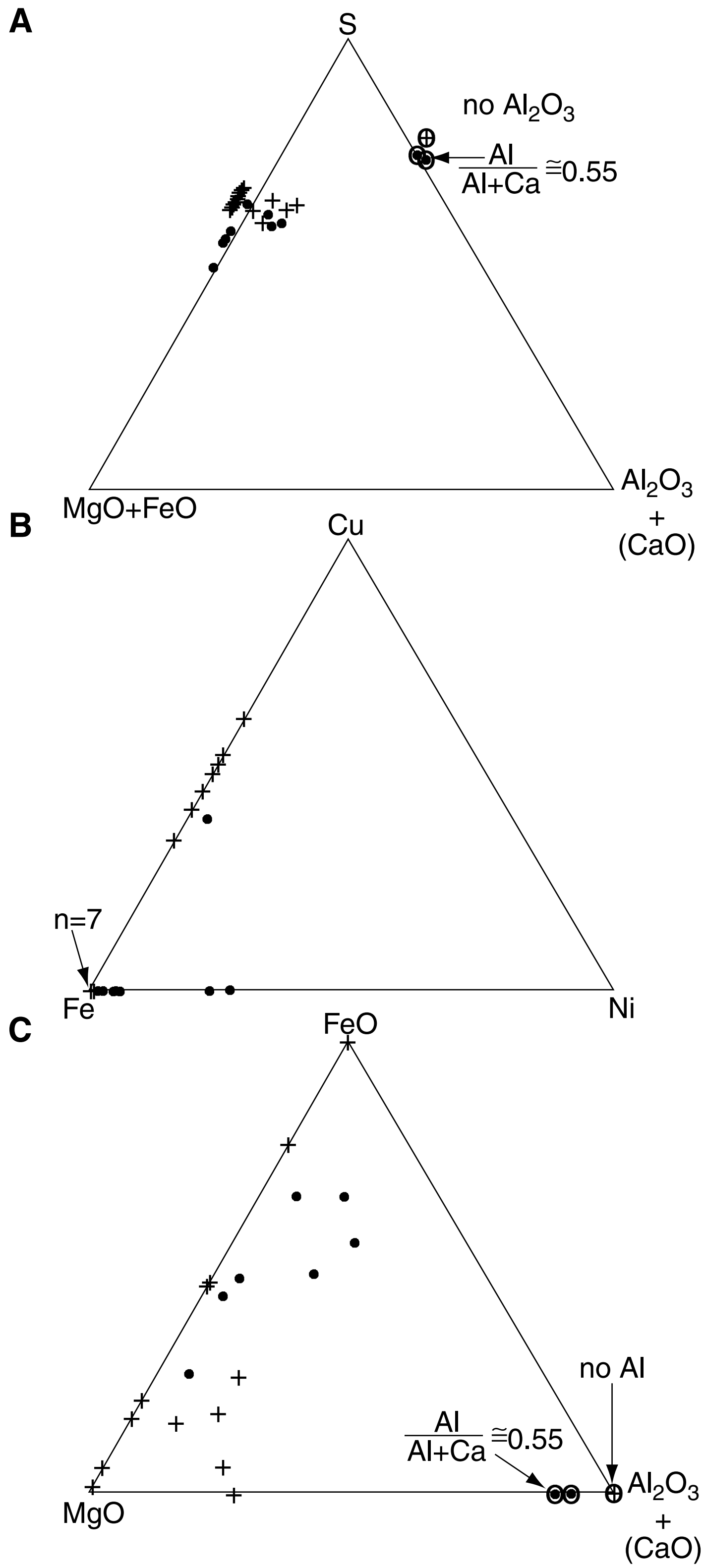

Table T1. Analyses of tochilinite and related minerals, Hole 1068A.

Core, section:	24R-1	21R-2	21R-2	21R-2	21R-2	21R-2	21R-2	21R-2	20R-6	20R-6
Interval (cm):	34	110	110	110	110	110	110	110	89	89
Piece:	5	1	1	1	1	1	1	1	12	12
Characteristic:	Cu rich	Ni rich	Ni rich	Tochilinite	Tochilinite	Tochilinite	Tochilinite	Tochilinite	Ca rich	Tochilinite
S	17.49	19.98	20.12	19.00	17.98	21.28	21.05	18.39	23.61	23.22
Fe	17.83	25.48	27.04	31.97	29.71	34.67	35.76	30.15	37.68	37.53
Co	0.00	0.02	0.00	0.15	0.15	0.29	0.10	0.17	0.00	0.00
Cu	13.02	0.05	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Ni	1.26	9.73	8.42	1.01	1.51	2.17	0.80	1.81	1.52	0.02
SiO_2	0.00	0.15	0.34	0.62	1.03	0.68	0.47	0.94	0.09	0.34
Al_2O_3	2.31	4.61	5.10	1.19	1.06	1.32	3.21	1.21	8.60	8.94
FeO	22.21	6.08	3.59	10.70	11.65	4.02	2.94	10.00	0.00	0.00
MgO	16.10	16.53	17.53	16.58	17.15	17.76	18.62	18.11	1.49	1.13
CaO	NA	NA	NA	NA	NA	NA	NA	NA	7.98	7.92
Total:	90.22	82.64	82.14	81.21	80.23	82.19	82.95	80.77	80.96	79.10
Sulfur/oxide:	0.72	1.06	1.07	1.02	0.92	1.27	1.16	0.94	2.01	1.95
Sulfide composition, mol.										
Fe	0.59	0.73	0.77	0.97	0.95	0.94	0.98	0.94	0.96	1.00
Ni	0.04	0.27	0.23	0.03	0.05	0.06	0.02	0.05	0.04	0.00
Cu	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00
Oxide composition, mol.										
Mg	0.67	0.32	0.21	0.51	0.53	0.27	0.18	0.47	0.11	0.08
Fe	0.27	0.49	0.56	0.44	0.44	0.66	0.66	0.48	0.00	0.00
Al	0.06	0.19	0.23	0.04	0.04	0.07	0.16	0.05	0.48	0.51
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.41

Notes: All Ni, Co, and Cu are assigned to sulfide. FeO is calculated from Fe not assigned to sulfide. NA = not available. Values are reported in weight percent, unless otherwise marked as mol. Mol. = molecular percent.