

Native nickel in the TAG hydrothermal field sediments (Mid-Atlantic Ridge, 26°N): Space trotter, guest from mantle, or a widespread mineral, connected with serpentinization?

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[1] Tiny metallic particles have been found in the sediments of the Trans-Atlantic Geotraverse (TAG) hydrothermal field, Mid-Atlantic Ridge (MAR). The metallic grains are almost pure Ni and have compositional and structural characteristics similar to those of other terrestrial metallic Ni⁰ occurrences. Native nickel grains, documented here for the first time in oceanic sediments, appear in calcareous oozes intercalated with metalliferous layers, layers with bedrock rubble, and sporadically scattered cosmic microspherules. There are three possibilities for the metallic Ni⁰ genesis: (1) cosmic, (2) lower mantle at the core-mantle boundary, or (3) upper mantle/lower crust. The flake-like appearance of the Ni⁰ grains rules out cosmic ablation origin. No unequivocal evidence was found that the Ni⁰ particles could have formed under high-pressure conditions similar to those at the core-mantle boundary. Ni⁰ formation through seawater serpentinization of the upper mantle/lower crust is the most plausible mechanism. At the slow spreading MAR, seawater penetrates down through highly fractured crest zone and serpentinizes the olivine and pyroxene of the upper mantle/lower crust ultramafics/mafic. Serpentinization results in the generation of highly reduced volatile species: H₂ and hydrocarbons. In such an extremely reduced environment, Fe and other transition metals (Co, Ni, Cu, Zn) released from olivines and pyroxenes tend to appear as native metals if fS_2 approaches 0. The lightened serpentinized blocks uplift and expose the serpentinized ultramafics/mafic at the rift valley's walls. I speculate that tectonic movements and weathering could liberate the native metallic grains scattered in the serpentinized rocks, which may then have been dispersed in the proximate sediments by near-bottom currents.

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1. Introduction

[2] The occurrence of elements in zero-valent state in nature has long attracted the attention of scientists [Ramdohr, 1975]. Debatable still remain the finds of native lithophile elements like Al⁰ [Okruhin *et al.*, 1981], Ti⁰ [Distler *et al.*, 2004] and Si⁰ [Robinson *et al.*, 2004]. Chalcophile (Cu, Zn, Pb) and siderophile (Fe, Co, Ni, PGE) elements are often found in native state, and their occurrences do not provoke particular discussions. Nickel-iron alloy grains attributed to either cosmic [Bi *et al.*, 1993] or mantle [Bai *et al.*, 2000] input are frequently described, whereas reports on pure native Ni⁰ are rare.

[3] Here I report on the composition and origin of grains of metallic Ni found in the course of a study for cosmic

microspherules from the sediments of the TAG hydrothermal field (26°N MAR). The study is based on only two occurrences found in no close relation with the host rocks, which sets some limitations to my interpretation. However, the uniqueness of the samples (they are the only native Ni⁰ occurrences found so far in oceanic sediments) justifies their documentation.

2. Geological Setting

[4] The TAG hydrothermal field [Rona *et al.*, 1986] lies on the rift valley floor of the slow spreading MAR between the Atlantis and Kane fracture zones [Sempéré *et al.*, 1990] (Figure 1a). It comprises three sulphide mounds: one active and two dead [Rona *et al.*, 1993; Humphris *et al.*, 1998] (Figure 1b). The rift valley at this latitude (26°N) is characterized by an asymmetric structure: The east wall is higher and steeper than the west wall [Rona *et al.*, 1986, 1993] and exposes the sheeted-dike complex and gabbro layer on its lower part [Lisitsyn *et al.*, 1989]. The uplift of

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the east wall is believed to be a result of serpentinization of the upper mantle rocks [Zonenshain *et al.*, 1989]. Talus of variably altered gabbroic clasts sporadically covers the foot of the east wall. The active high-temperature sulphide mound is located east of the spreading axis at the juncture between the rift valley floor and the east wall. It is a large edifice with a black smoker complex surrounded by a wide platform with a group of white smokers and an apron of metalliferous sediments [Rona *et al.*, 1986, 1993]. Two inactive sulphide deposits (Mir and Alvin) occur on the

lower east wall of the rift valley and are undergoing extensive mass wasting [Lisitsyn *et al.*, 1989; Rona *et al.*, 1993]. The Mir relict hydrothermal zone showing various stages of weathering is situated between the low-temperature zone, some 300 m higher on the wall, and the active high-temperature sulphide mound [Rona *et al.*, 1993]. Several basaltic lava domes are situated around sulfide mounds. The sediment cover surrounding the Mir mound is composed of nanofossil-foraminiferal and foraminiferal-nanofossil oozes with intercalations of metalliferous sediments and layers rich in basement rocks rubble (Figure 1c).

3. Materials and Methods

[5] The materials I used in this study were subsamples of gravity core 15AMK 1891 taken close to the Mir zone during the 15th cruise of the Russian R/V *Akademik Mstislav Keldysh* (IO-RAS) in 1988 [Lisitsyn *et al.*, 1989] (Figure 1b).

[6] The samples were hermetically stored at room temperature in polythene boxes (100 mL) following collection. Special care was taken to prevent natural or anthropogenic contamination of the samples. They were separated into size fractions (decimal scale) by wet sieving with distilled water (to remove interstitial salts) in a controlled lab environment ($\sim 20^{\circ}\text{C}$).

[7] I aimed to investigate the cosmic microspherules in these sediments. The expected low contents of these particles prevented the use of routine bulk mineralogical techniques for mineral diagnostics. Since the investigation of scarce microspherules from the fine (<0.10 mm) sediment fractions was difficult, I examined only the coarse fractions (>0.10 mm) under a stereomicroscope. Uncommon mineral grains, which attracted my attention, were handpicked with a steel needle for further studies. The micromorphology, size, and chemical composition (point analyses; semiquantitatively) of the selected metallic grains were investigated by scanning electron microscope (SEM) Jeol T-300 with a Link 860–500 energy-dispersion spectrometer (EDS) ($U = 20$ kV; electron beam diameter of $1\ \mu\text{m}$; ZAF/PB software). Precise chemical composition (point analyses onto polished sections) was determined by employing a Cameca microprobe unit ($U = 15$ kV; $I = 15$ nA; electron beam diameter of $1\ \mu\text{m}$; detection limits 0.1 wt%) using the following standards and X-ray lines:

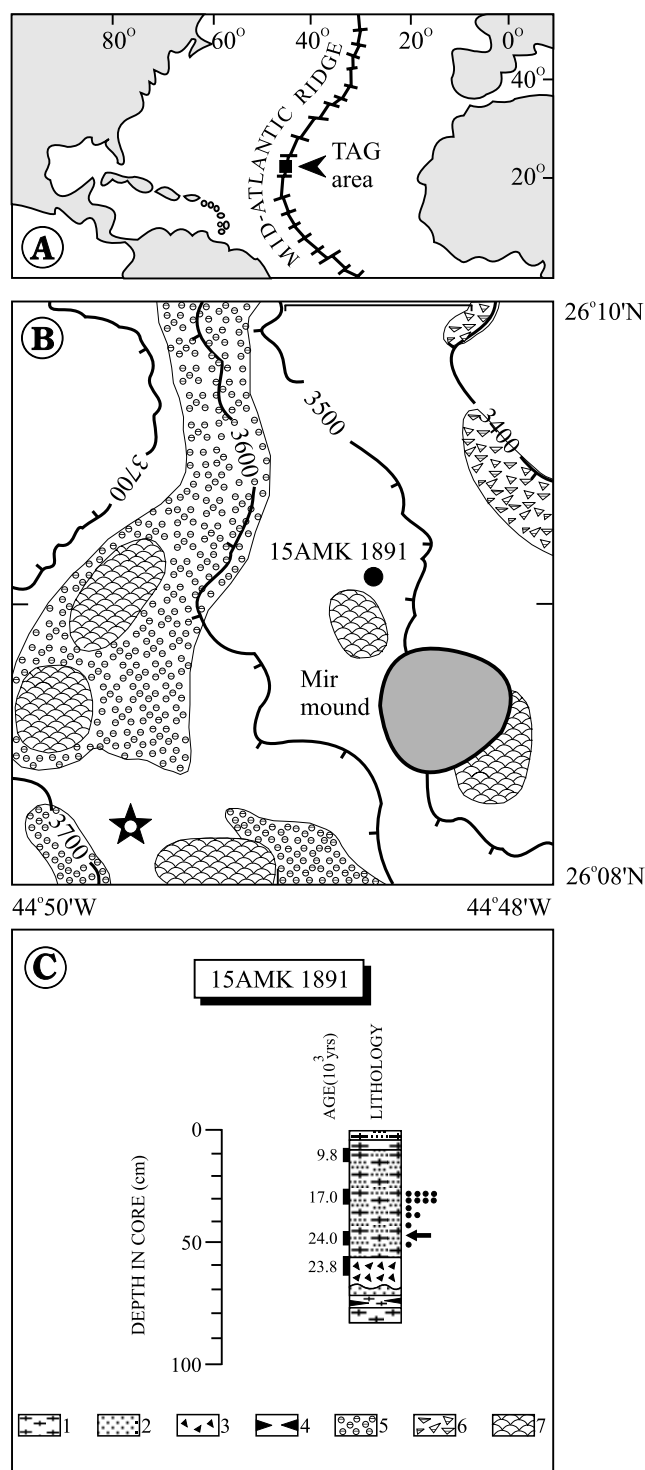


Figure 1. (a) Index map showing the location of TAG area, MAR. (b) Bathymetric map (based on work by Lisitsyn *et al.* [1989] and Rona *et al.* [1993]) of the investigated area showing the position of the active high-temperature sulphide mound (star) and inactive Mir mound (bar in upper right is 1 km long). (c) Stratigraphic section (based on work by Lisitsyn *et al.* [1989]) showing the lithology, ¹⁴C age determinations, number and location of Fe microspherules (solid circles) and native Ni⁰ (black arrow) found in the studied core. Legend: 1, nanno-foram and foram-nanno oozes; 2, disseminated hydrothermal components (sulfides, Fe- and Mn-oxhydroxides, quartz); 3, clastic sulfide-oxhydroxide layer; 4, nontronitic lenses; 5, pillow talus; 6, talus with gabbroic clasts; 7, basaltic domes.

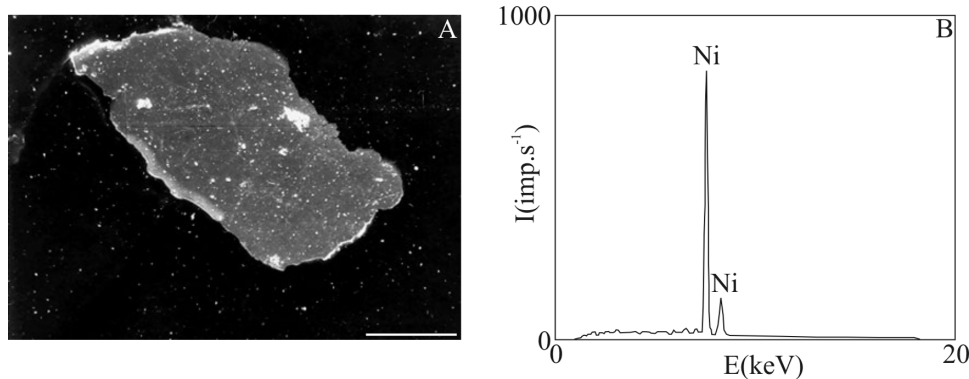


Figure 2. (a) SEM microphotograph (backscattered electron image; scale bar equal to 100 μm) and (b) EDS spectrum of a native Ni^0 particle (H105III.S41).

pure synthetic Ni (Ni K_{α}), pure synthetic Fe (Fe K_{α}), pure synthetic Co (Co K_{α}), and quartz (Si K_{α}).

[8] The X-ray diffraction patterns of the metallic grains were obtained with a 57.3 mm Gandolfi camera employing Ni-filtered Cu K_{α} radiation without internal standard ($U = 40$ kV; $I = 19$ mA).

4. Results and Discussion

[9] Both grains of metallic Ni^0 (Figure 2a) are flat, flake-like, with irregular outlines, size $200 \times 400 \mu\text{m}$, silver white, with metallic luster under the stereomicroscope and white, isotropic, with very high reflectivity under the ore microscope. The mineral is magnetic and hard but presents no difficulty in yielding a good polish. It is almost pure Ni (Figure 2b) with traces of Fe, Co and Si (Table 1), and has a face centered cubic lattice with $a_0 = 3.532 \text{ \AA}$ (Table 2).

[10] Ni-Fe alloy particles with Ni content approaching 100 wt% have been found in diverse terrestrial environments, in a variety of cosmic objects interacting with the Earth, and produced in lab experiments with rocks (Table 1). They all fall at the Ni apex of the ternary Ni-Fe-Co diagram, and no clear compositional trend could be found to discriminate their source. The composition and crystal structure of studied Ni^0 particles do not put any constraints on their origin: they are stable in quite a wide temperature range (Figure 3). What draws the attention is that most of the terrestrial native Ni^0 occurrences are from serpentinized rocks but not from hydrothermal deposits (Table 1).

[11] Metallic Ni occurrences described here were not found in intimate intergrowth with bedrocks, which put some doubt on their natural genesis. However, they are from a layer with pretechnogenic age (24,000 years B.P.; Figure 1c), and the anthropogenic contamination of this sediment through sailing, wrecks, etc., can be excluded. Contamination during sampling, onboard, and lab treatment is hardly possible as well, since the metallic parts of all the sampling devices, tools, instruments, and lab ware were from stainless steel with no pure Ni parts. Moreover, special precautions during the core sampling and sample treatment have been undertaken. Studied Ni^0 particles contain 0.2–0.7% Si, which is never used as alloying component in synthetic Fe-Ni alloys.

[12] Metallic Ni^0 occurs along with scattered sulfide and sulphate minerals in the sediment. This might imply a

hydrothermal origin of the Ni^0 grains. Metallic Ni^0 precipitation from hydrothermal fluid would require lack of reactive sulfur in the fluid. Otherwise, the dissolved Ni would precipitate as Ni sulfide or oxide upon seawater/fluid mixing. This is not the case of the TAG hydrothermal fluids rich in reactive sulfur [Edmonds *et al.*, 1996]. Hence a hydrothermal origin of Ni^0 is not likely.

[13] Metallic Fe-Ni is nearly ubiquitous in extraterrestrial objects: meteorites, lunar rocks, and interplanetary dust particles. In these objects, metallic Fe-Ni most commonly occurs as spheroids, rounded particles, or coarse anhedral grains. Ni-Fe alloy with Ni > 90% forms the metallic cores of magnetic cosmic spherules (impact and nonimpact) found in deep-sea sediments, ice caps and ancient sedimentary successions on Earth [El Goresy, 1968; Kelly *et al.*, 1974; Bi *et al.*, 1993]. Ni^0 particles from TAG appear in sediment situated among layers rich in cosmic microspherules (Figure 1c). This begs the question about the cosmic nature of the TAG Ni^0 . In a study of the TAG cosmic spherules (V. M. Dekov *et al.*, The fifth step of “Dong Bi”, manuscript in preparation, 2006) we found no metallic core in all sectioned specimens. Thus I am not able to compare the composition of Ni^0 particles with that of the TAG probable spherule cores. This, however, does not completely rule out the possibility of cosmic genesis of Ni^0 particles. A cogent argument against the cosmic origin of the TAG Ni^0 is their form: flat, flake-like in contrast to the spherical, drop- or tear-like shape of the extraterrestrial Fe-Ni particles [El Goresy, 1968; Kelly *et al.*, 1974; Czajkowski, 1987; Bi *et al.*, 1993].

[14] Fe-Ni alloy is the most abundant component in Earth’s core [Birch, 1952]. The mantle excess of Ni and some siderophile elements compared to the theoretical expectations is known as the “siderophile element problem.” The most plausible model for explaining this problem is that the mantle, which has given birth to the core, subsequently receives additional material from the core which does not behave as a passive, sealed siderophile element reservoir [Walker, 2000]. Mantle plumes reaching the lithosphere can develop from boundary layers either at depths of 660 km (lower/upper mantle) or at 2900 km (core-mantle) [Cserepes and Yuen, 2000; Cserepes *et al.*, 2000]. In view of the inferred core-mantle mass exchange and core-mantle boundary plumes it is a reasonable hypothesis that Ni-Fe alloy in the josphinite might have derived from

Table 1. Chemical Composition of Native Ni⁰ and Ni-Fe Alloys^a

Object and area of investigation	Present Study	Ramdohr [1967]	Challis [1975]	Simton [1976]	Vasil'ev et al. [1976]	Graham [1978]	Hudson and Travis [1981]	Pakkanen and Luukkonen [1995]	Gorsikov et al. [1996]
Metallic particles								Chlorite schist, Kauninvaara ultramafic body, Late Archaean Suomussalmi greenstone belt, Eastern Finland	Carbonado, kimberlite pipes, Yakutiya, Russia
Sediments, TAG hydrothermal field, MAR 26°N									
Heazlewoodite vein, Bogota, near Canala, New Caledonia									
Stream sediments, Jerry River, South Westland, New Zealand									
Serpentinites, Red Mountain, New Zealand									
Serpentinites, Kitoy River, East-Sayan ultrabasic belt, Russia									
Serpentinized peridotite, Mount Clifford, Western Australia									
Ores, Naime pyrite deposit, South Australia									
Native Ni ⁰									
Sample	HI05III.S41								
Ni	98.99, 98.10	>98	96.30	37031	85.3	>88	96.41	934663	98 - 99
Fe	0.60, 1.00	<2	1.77	8.51	14.7	~5.5	1.41	92.2, 93.0, 93.3, 93.3, 92.7	2 - 1
Co	0.10, 0.10	<2	0.69	nd	0.76		0.45	0.29, 0.20, 0.17, 0.28, 0.25	- ^b
S	-	-	-	-	-	-	-	nd, ^c 0.03, nd, 0.02, nd	-
Cu	-	-	-	nd	0.48	-	1.51	0.01, nd, nd, nd, nd	-
Si	0.20, 0.70	-	-	-	-	-	-	5.77, 5.73, 5.14, 6.33, 6.05	-
Zn	-	-	-	-	-	-	-	- ^{d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z}	-
Ag	-	-	-	-	-	-	-	nd, 0.02, nd, 0.04, 0.05	-
Hg	-	-	-	-	-	-	-	0.05, nd, 0.10, 0.01, 0.11	-
Bi	-	-	-	-	-	-	-	nd, 0.01, 0.26, nd, nd	-
Au	-	-	-	-	-	-	-	0.04, 0.03, nd, nd, nd	-
Se	-	-	-	-	-	-	-	nd, nd, nd, 0.01, 0.01	-
Te	-	-	-	-	-	-	-	0.09, 0.09, 0.10, 0.15, 0.14	-
Sb	-	-	-	-	-	-	-	0.05, nd, nd, 0.17, nd	-
As	-	-	-	-	-	-	-	nd, nd, nd, nd, 0.03	-
Total	99.89, 99.90	>98	98.76	97.6	101.24	>93.5	99.78	98.46, 99.10, 99.11, 100.41, 99.45	100
Object and area of investigation									
podiform chromitites, Luobusa ophiolite, southern Tibet, China									
Greenland ice									
Impact magnetic spherules, soil, Tunguska Fall, Russia									
metalliferous core of magnetic spherule									
Ni-Fe alloy nucleus of magnetite spherule									
Sample	2-7	42	2				1719		
Ni	92.18	96.90	90	90, 95	95.0, 95.0	97.9, 96.6	94.30	OW-N45, OW-N52, OW-N10, OW-N5	96
Fe	2.42	1.80	10	5.7, 4.9	5.7, 4.9	2.1, 3.4	4.45	99.62, 99.94, 100.53, 100.68	4
								1.10, 0.38, 0.17, 0.10	
Metallic particles									
native Fe-Ni									
Ni-Fe alloy									
fusion crust, Cherokee Springs (LL6)									
Chlorite schist, Kauninvaara ultramafic body, Late Archaean Suomussalmi greenstone belt, Eastern Finland									
Pleistocene sediments, Alberta, Canada									
Jurassic hardgrounds									
Ni-Fe-Mg-Si-O-H-S system, experimental serpentinization of olivine by NaOH in a S-free system									
Ni-rich awaruite									
Ni-Fe cores of deep-sea spherules									
cosmic Ni-Fe alloy spherules									
M. Bussell (personal communication, 1972), as cited by Graham [1978]									
impactite samples, Barringer Meteorite Crater, Arizona, USA									
experimental dehydration of serpentine nickel ore									
impacritic metallic particles									
Bi et al. [2000]									
El Goresy [1968]									
Florenskiy et al. [1969]									
Kelly et al. [1974] ^d									
Fitilipidis [1985]									
Czajkowski [1987]									
Bi et al. [1993]									
Genge and Grady [1999]									

Table 1. (continued)

	Bai et al. [2000]	El Goresy [1968]	Florenskiy et al. [1969]	M. Bussell (personal communication, 1972), as cited by Graham [1978]	Kelly et al. [1974] ^d	Filippidis [1985]	Czajkowski [1987]	Bi et al. [1993]	Genge and Grady [1999]
Co	-	0.20	1.6	0.3, 0.7	-	-	0.32	nd, nd, 0.02, 0.03	nd
Si	-	-	-	-	-	-	-	0.05, 0.05, 0.07, 0.11	-
Mn	-	nd	-	-	-	-	0.06	0.05, 0.01, 0.02, 0.05	-
Cr	-	nd	-	-	-	-	0.04	0.01, 0.02, 0.01, 0.03	-
Cu	5.39	-	-	-	-	-	-	-	-
Total	99.99	98.9	101.6	101.0, 100.6	100.0, 100.0	99.17	100.86, 100.45, 100.90, 101.11	100	

^aComposition values in wt %.^bNot analyzed.^cNot detected.^dData from their Figures 5 and 6.

the primitive mantle at the core-mantle boundary, transported in convecting mantle material and subsequently incorporated into depleted mantle of lithosphere during plate accretion [Bird and Weathers, 1979]. This hypothesis has focused much attention and spawned controversy (Bird and Weathers, [1975], Dick and Gillette [1976], and others since). However, the helium isotopic composition of unaltered native Ni-Fe from josephinite is consistent with its formation in either an upper mantle source or during serpentinization of the Josephine peridotite [Poreda et al., 1990]. Accordingly, I do not suggest the TAG metallic Ni⁰ has been transported from the lower mantle by a plume and incorporated into the oceanic crust during seafloor spreading.

[15] The abundance of Ni in the upper mantle is far too high to have been in equilibrium with the Fe-rich metal that formed the Earth's core, at least at the present T and P of the upper mantle [Richet et al., 1966]. The corollary of this is that on reducing an upper mantle rock assemblage, Ni-rich metal will eventually precipitate. This has been experimentally observed [Boland and Duba, 1986]:



[16] Thus the upper mantle origin of the TAG Ni⁰ occurrences seems possible. Upper mantle rocks with accessory native Ni⁰ particles could be tectonically emplaced in the TAG rift zone, crop out the rift valley walls, and liberate the Ni⁰ particles along with bedrock shards upon tectonic disintegration or weathering with subsequent dispersal of native Ni⁰ in nearby sediments. The shape of the Ni⁰ grains indicates that it is detrital and must have a source within the rift valley.

[17] The host rocks for almost all known occurrences of terrestrial native Ni⁰ have been serpentinized (Table 1). The common occurrence of native metals in serpentinized peridotites [Ramdohr, 1975] casts some doubts as to whether they originated at the core-mantle boundary [e.g., Bird and Weathers, 1975]. Ramdohr [1975] concluded that native metals in serpentinites are much more abundant than is commonly recognized and are often overlooked because of their extremely fine grain size.

[18] Considerable interest has arisen over the occurrence of native metals in serpentinized peridotites [Frost, 1985; Alt and Shanks, 1998; Früh-Green et al., 2004]. Nickel [1959] studied native Ni-Fe of a serpentinite belt in an attempt to determine whether or not Ni in this alloy was added during serpentinization or was already present in primary minerals of un-serpentinized peridotite. His study indicated that the Ni content of primary silicates is sufficient for the formation of Ni-Fe alloy and that serpentinization serves only to reduce Ni to the elemental state and concentrate it into small metal blebs.

[19] Experiments [Krishnarao, 1964; Persikov et al., 1986] showed that Ni-Fe alloy and Ni⁰ could be produced in a reducing environment by H₂ acting as a reducing agent. In an experimental study, Philippidis [1985] investigated the serpentinization of Mg, Fe, Ni olivine. Nickel content in one of the products of hydrothermal hydration of olivine, Ni-Fe alloy, approaches 100% when fS₂ approaches 0. The Ni content of the Ni-Fe alloy is interpreted as being derived

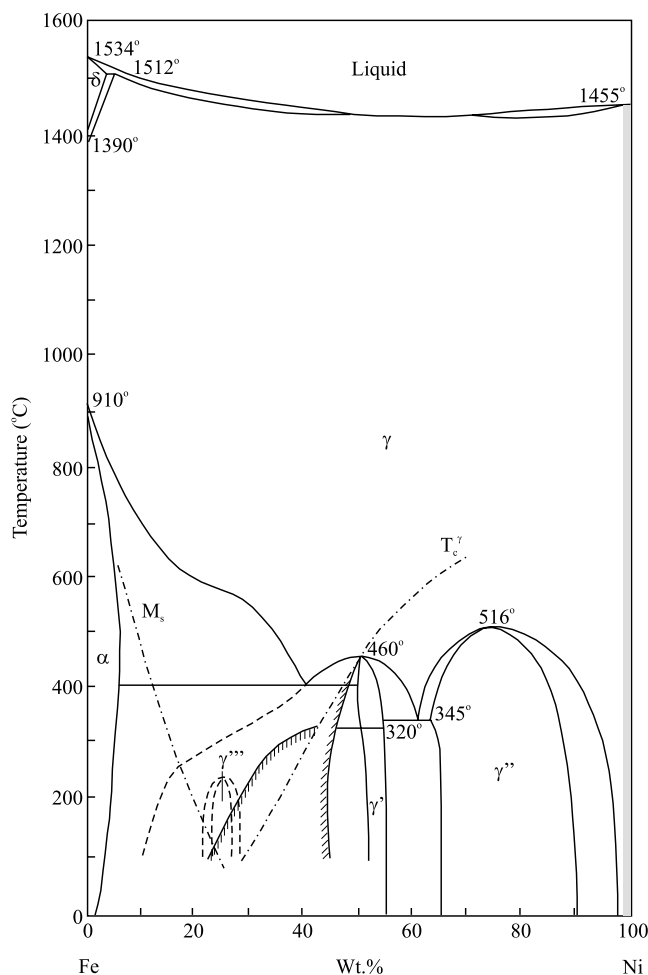


Figure 3. Fe-Ni phase diagram [after Hansen and Anderko, 1958; Reuter et al., 1988; Fröh-Green et al., 2004]. Definitions are α , kamacite (BCC structure); γ , taenite (disordered with a FCC structure); γ' , tetrataenite (FeNi, ordered tetragonal structure); γ'' , awaruite (Ni₃Fe, ordered); γ , Fe₃Ni (ordered); M_s , martensite start boundary; T_c^γ , Curie temperature (see cited references for further details). The vertical shaded region shows the composition range of studied native Ni⁰ particles.

from both primary silicates and sulfides. Serpentinization produces a conversion of silicate Ni into metallic or sulfide Ni depending on two variables: fO_2 and fS_2 . Metallic Ni formation requires fO_2 at or below iron-magnetite oxygen buffer and fS_2 at or below iron-troilite buffer [Filippidis, 1985].

[20] Along slow and ultraslow spreading ridges, mantle and lower crust peridotites and gabbros are exposed at shallow structural levels. Exothermic serpentinization reactions between seawater and mafic/ultramafic rocks generate H₂- and CH₄-rich fluids and may drive low-temperature hydrothermal circulation [Kelley et al., 2001; Fröh-Green et al., 2004; Kelley et al., 2005]. Hydrothermal activity also induces serpentinization of the oceanic crust at slow spreading ridges [Palmer, 1996]. Low-T (<150°C) downwelling limbs of the hydrothermal convection cell penetrate deep in the crust and upper mantle and serpentinize the basic/

ultramafic units. The associated hydration of the crust reduces its density, which results in uplift, leading to substantial elevation of the rift valley walls. This effect is greatest in the vicinity of large hydrothermal fields [Palmer, 1996]. Along the MAR, CH₄, and H₂ anomalies over axial ultramafic sites are common [Charlou and Donval, 1993; Charlou et al., 1998; Charlou et al., 2002] and point to the association of high-temperature hydrothermal activity, mantle degassing indicative of ongoing serpentinization process generating the large H₂-CH₄ fluxes observed at the ridge axis. The hydration of olivine and orthopyroxene with conversion of Fe(II) in silicates to Fe(III) in magnetite during serpentinization (300°C, 500 bars) leads to production of H₂ (even >40% of the total gas volume [Charlou et al., 2002]) and conversion of dissolved CO₂ to reduced-C species including CH₄ in mafic/ultramafic rocks through Fischer-Tropsch type reactions [Berndt et al., 1996]. In addition to hydration of olivine and orthopyroxene, H₂ may be generated by a high-T reaction between seawater and silica radicals and by outgassing from the mantle rocks under stress as well [Charlou et al., 1998].

[21] In the extremely reducing condition of serpentinization the transition metals (Co, Ni, Cu, Zn) inherited from primary olivine and pyroxene will display a tendency to appear instead of or in association with Fe as native metals if fS_2 is low. The redox conditions of serpentinization approach those needed to stabilize native metals [Berndt et al., 1996].

[22] There are no reported ultramafic rocks cropping out on the walls of the TAG rift valley. Submersible observations at the foot of the highly uplifted TAG east wall documented gabbros [Zonenshain et al., 1989], which appeared to be quite numerous along the MAR rift valley [Bougault et al., 1993]. CH₄-H₂-bearing fluids found in gabbros from the South-West Indian Ridge [Kelley et al., 2002] suggest that the gabbroic layer 3 of the oceanic crust may represent a potential reservoir for abiogenic reduced gasses in mid-ocean ridges. Moreover, this reduction accompanies the formation of Fe-Ni alloys [Kelley et al., 2002]. The talus of altered gabbroic clasts at the foot of the TAG east wall nearby the sample site (Figure 1b) and the presence of a CH₄-enriched hydrothermal plume believed to have its origin on the rift valley's east wall [Nelsen and Forde, 1991] provide evidence for ongoing serpentinization of the exposed layer 3 at TAG. It is plausible these serpentinization processes lead to formation of native Ni⁰ and Ni-Fe alloys in the mafic/ultramafic plutonic complex of layer 3. Disintegration of the outcropping serpentinized rocks during tectonic movements (eastern rift valley wall is seismically very active [Kleinrock and Humphris, 1996]) or seafloor weathering may release tiny Ni⁰ grains scattered in the parent rock. Near-bottom currents could presumably disperse the metallic grains within adjacent sediment.

[23] Much still remains to be learnt about the extent of native metal formation in the upper mantle/lower crust rocks subjected to serpentinization by seawater. Such processes are global and influence a wide range of submarine environments: forearcs, mid-ocean ridges, and transform faults [Kelley et al., 2005]. Any of these tectonic settings could produce native metals dispersed in the bedrocks. We may tentatively estimate the scale of Ni⁰ formation in the upper mantle/lower crust through hydrothermally induced serpen-

tinization at the TAG site. The volume of serpentinite inferred to have been produced during the lifetime of the TAG system (12.5×10^3 years [Lalou *et al.*, 1993]) is $1.2\text{--}3.8 \times 10^9$ m³ [Palmer, 1996]. Taking the serpentinite density of $\sim 2.55 \times 10^6$ g/m³ [Bonatti, 1976] and considering that about 300 ppm Ni is released during serpentinization of a given weight of peridotite [Frost, 1985], about $0.9\text{--}2.9 \times 10^6$ t metallic Ni⁰ may have been produced at TAG during its lifetime.

[24] The evidence presented here is another piece in the global picture that links serpentinization of the upper mantle/lower crust ultramafic/mafic rocks and native Ni⁰ formation. The metallic Ni⁰ occurrences found in the TAG sediments should be considered a product of serpentinization of the lower crust gabbros pending unequivocal evidence they could have formed under high-P conditions similar to those at the core-mantle boundary.

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