[AMERICAN JOURNAL OF SCIENCE, VOL. 276, MARCH, 1976, P. 241-274]

American Journal of Science

MARCH 1976

JOSEPHINITE: A UNIQUE NICKEL-IRON

ROBERT I. BOTTO and GEORGE H. MORRISON*

Department of Chemistry, Cornell University, Ithaca, N.Y. 14853

ABSTRACT. Josephinite, terrestrial native nickel-iron from Josephine County, southwest Oregon, is uniquely different from nickel-iron metal (awaruite) found in any other of its numerous serpentinite occurrences worldwide. Josephinite is actually a rock containing two or more native metal phases intergrown with silicate minerals. This paper describes specimens that contain fine crystallographically oriented intergrowths of nickel-rich taenite (γ–Fe,Ni) and awaruite ($FeNi_3$) with andradite garnet. This mineral association has not been reported from any other locality.

Metallographic, mineralogical, and chemical analyses performed indicate that josephinite probably formed over a range of temperatures (from about 500° to below 350°C) in a chemically evolving serpentinization environment. Specimens displaying the taenite–awaruite–andradite intergrowths probably formed above about 450°C. The original metal was a single phase, taenite. Specimens formed at the lower temperature (below 375°C) end of this range contain only awaruite and display associated minerals, textures, and a chemical composition more typical of other occurrences of this mineral.

Our extensive study differentiates between two contrasting metallogenic regimes of serpentinization. Higher temperatures and more strongly reducing conditions resulted in the establishment of a metallogenic environment dominated by arsenic, under which nickel–iron, containing trace elements carried along by arsenic, was deposited with secondary arsenide minerals. At lower temperatures, the formation and chemistry of josephinite was dominated by the influence of sulfur, as in the many other well documented occurrences of native metals formed during serpentinization.

INTRODUCTION

Josephinite, terrestrial native nickel-iron from Josephine County, southwest Oregon, was first described by W. H. Melville in 1892. Since then, it has been an object of curiosity and occasional mineralogical study.

Native nickel-iron occurs in many localities worldwide and is always associated with serpentinized ultramafic rocks (Krishnarao, 1964). The name awaruite was given to the first reported occurrence of native nickel-iron at Awarua Bay, New Zealand in 1891 (Ulrich, 1891) and is considered by several authors to have precedence over local names for this material from other localities such as souesite (British Columbia), bobrovkite (Ural Mountains, USSR), and josephinite which have appeared in the literature. Josephine County, however, is the only locality where specimens of native nickel-iron larger than a few millimeters have been found. Josephinite specimens weighing several ounces, although rare, can be obtained for study, and a specimen weighing 100 pounds has been reported (Palache, Berman, and Frondel, 1944). Grains of native nickel-iron reported from other localities in stream placer deposits may be millimeters in size but rarely exceed 100 microns where observed in place in serpentinite (Nickel, 1959).

---

* Reprint requests should be addressed to G. H. Morrison at above address.

Awaruite is an isometric intermetallic compound in the nickel-iron system stable below 503°C and varying within limits about the composition $FeNi_3$ (Nickel, 1959). It has a face-centered cubic (FCC) lattice (cell constant $a_0 = 3.5522$ Å). However, nickel and iron atoms occupy preferred sites within the four atom unit cell. Iron atoms form a primitive cubic lattice while the three nickel atoms occupy the face-centered positions. The result is an ordered alloy with a primitive cubic unit cell (space group Pm3m) in addition to the FCC cell (space group Fm3m), a superlattice. Weak superlattice lines at larger d spacings than would be produced by the normal FCC nickel-iron lattice are observed in the X-ray powder pattern of awaruite (Nickel, 1959). If awaruite is heated above 503°C, it transforms to taenite, the disordered nickel-iron solid solution. Taenite has the FCC structure and a slightly larger cell constant ($a_0 = 3.5544$ Å) as awaruite of the same composition. However, it lacks the superlattice due to the absence of preferred positions for nickel and iron atoms within the unit cell.

The mineral associations and paragenesis of awaruite are well known from several recent studies of its occurrence in serpentinites (Nickel, 1959; Chamberlain and others, 1965; Ramdohr, 1950; Krishnarao, 1964). The close association of awaruite with nickel-sulfide minerals and magnetite indicates that it formed from chemical reactions taking place during the serpentinization of the host ultramafic rocks (Chamberlain and others, 1965). Several authors (Ramdohr, 1950; Jamieson, 1905; Krishnarao, 1964) have compared the mineralogy or composition of josephinite with native nickel-iron from other localities and have reported the alloys all to be similar in nature. However, the size and number of josephinite specimens available to them for study were small.

The present paper is the result of the study of a collection of about 40 josephinite pebbles from stream placers, ranging in size from 1 cm to over 10 cm in diameter. The collection also includes bits of metal in serpentinite found in bedrock in the source locality of josephinite (Dick, 1974). The authors have found the nickel-iron bearing pebbles from Josephine County to be distinctly different in mineral associations and composition from all other occurrences of nickel-iron (awaruite) that have been described. This paper focuses on josephinite. "Josephinite" will here be used as a rock name. The term awaruite will be used to describe the mineral as it occurs in serpentinite localities throughout the world or as one of the native metal phases in josephinite.

Geologic setting.—Josephinite is found in stream placers and upon the bedrock of Josephine Creek. The creek follows a belt of intensely sheared serpentinite at the bottom of a canyon separating Woodcock and Josephine Mountains, massifs of relatively unaltered harzburgite tectonite within the Josephine peridotite. The Josephine peridotite is an extensive thrust sheet of harzburgite-serpentinite covering about 1000 square km of southern Oregon and northern California. The regional geology of this area in the Klamath Mountains and the field occurrence of josephinite have been carefully studied by Henry Dick of Yale University (1974).

Josephinite-bearing placers were found by Dick to be closely associated with the serpentinite shear zone, especially where it had been intruded by diabase dikes. Field relations suggest that the development of the shear zone and its intrusion by the diabase dikes were closely spaced in time and were probably synchronous with the emplacement of the Josephine peridotite thrust sheet into the developing Klamath Mountains. The dikes have been dated by K-Ar and are Nevadan (150-155 m.y.) in age (Dick, 1973).

An area upstream from the Josephine Creek placers, where the shear zone crosses the south saddle of Woodcock Mountain, was selected by Dick as the probable source area for josephinite. This area is intruded by numerous diabase dikes, some of which are very large. The weathering and transport of josephinite from this area could explain its occurrence in Josephine Creek and in two other smaller creeks descending the opposite side of Woodcock Mountain. Outcrops in this area were sampled by Dick. Bits of metal up to 3 mm diameter were found in serpentine near the edge of the shear zone, where it was in contact with unaltered harzburgite. These specimens contained a unique andradite-nickel-iron intergrowth.

Sample description: mineralogy and metallography.—Josephinite pebbles have an exterior coating of brown serpentine. In spots the nickel-iron metal, along with magnetite and native copper, forms the specimen surface where the serpentine has been worn through by stream action. Specimens occur in sizes varying from tiny grains to masses weighing several pounds. Large specimens are generally spheroidal, ellipsoidal, or pod-shaped.

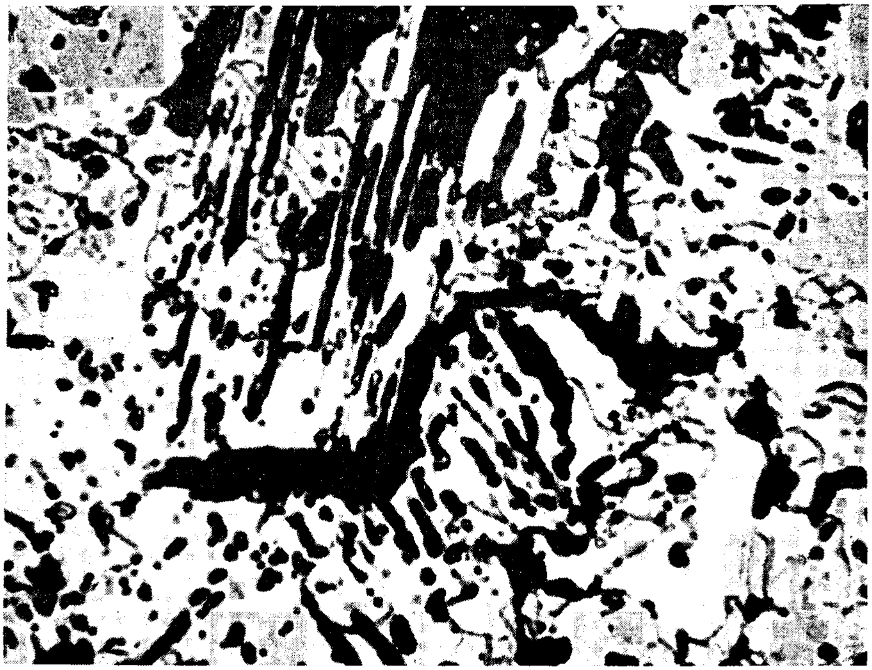
Nickel-iron and andradite.—The simplest and most persistent mineral assemblage in josephinite is a two-phase nickel-iron metal intimately intergrown with andradite garnet. Many specimens are composed of this assemblage entirely, except for their serpentine skins; in others nickel-iron and andradite intergrowth forms a central zone. This mineral association is apparently unique to josephinite. To our knowledge, andradite intergrown with nickel-iron has not been reported from any other locality.

Andradite was identified by powder X-ray diffraction and was found by electron microprobe analysis to have nearly the end-member composition (table 2). It is colorless to very light green with a refractive index (R.I.) of 1.860 to 1.886 and cell edge of $a_0 = 12.038 \pm 0.009$ Å. Ion microprobe analysis of the andradite in one specimen showed it to be anhydrous. Its appearance in the metal is striking (pl. 1-A). Blades and discontinuous blebs of garnet form cubic and octahedral patterns in the metal. The lamellar pattern is usually extremely fine, displaying garnet blebs and laminae widths in the micron and sub-micron size range. In some areas 1300 × magnification is not sufficient to resolve visually the garnet-metal intergrowth pattern. Larger anhedral masses (up to 1 mm diameter) of garnet also occur in the metal. These are surrounded by the

PLATE 1

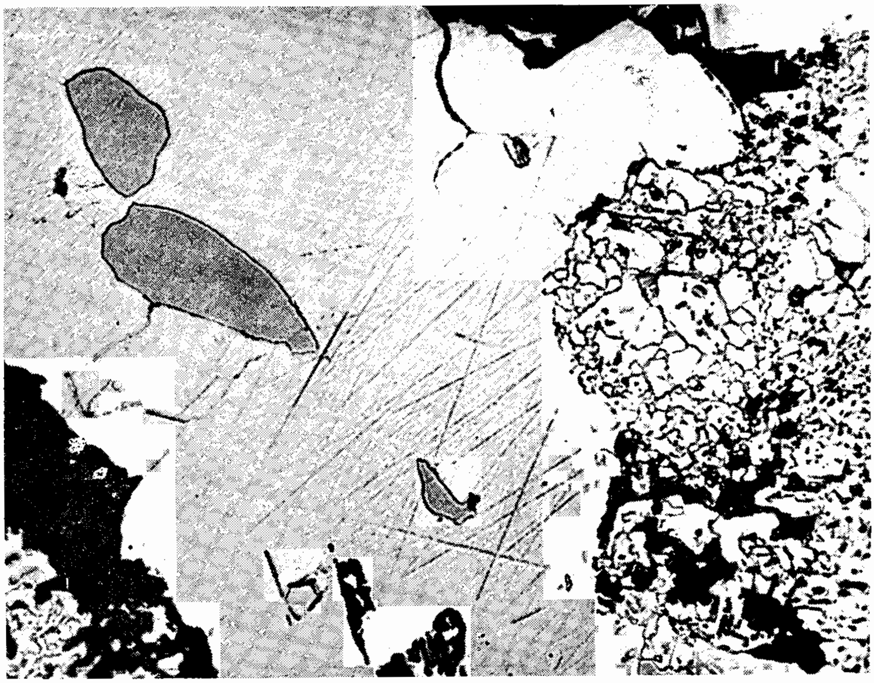
Various mineral assemblages and textures in josephinite. Photos taken on a Zeiss interference microscope in thallium (green) light. Specimen surfaces have been etched.

A. Geometric andradite–two-phase metal intergrowth pattern. Taenite–awaruite phase boundaries can be seen among the garnet blebs and lamellae. JCA 05 central zone, 1500×.



B. Taenite–awaruite phase boundary pattern. Taenite is incised and slightly darker gray. Very dark areas are andradite. Andradite lamellae and aligned discontinuous blebs can be seen crossing taenite–awaruite phase boundaries many places in this photo. JCA 01, 1500×.

PLATE 1

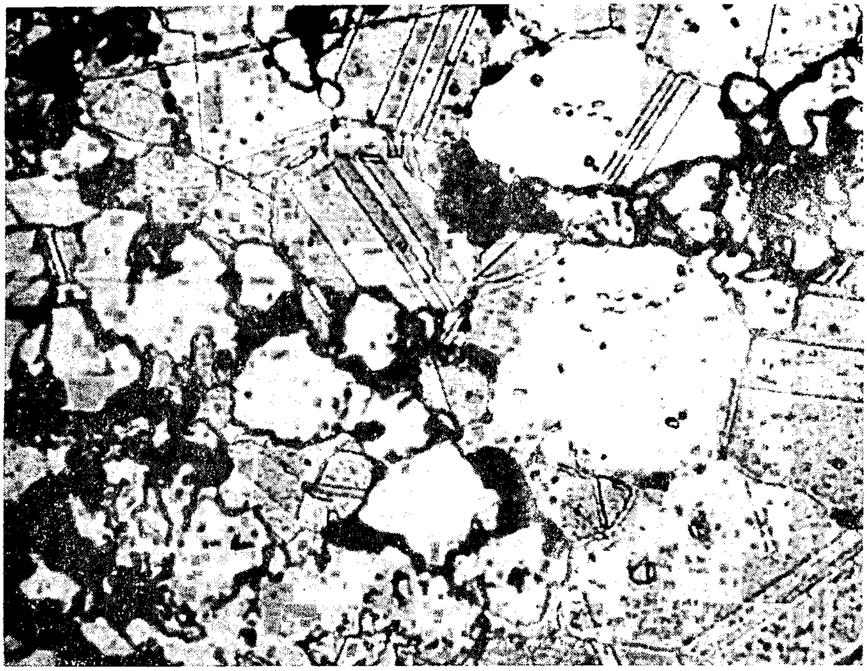


C. Nickel arsenide (Ni_5As_2 light gray) is included within a grain of solid awaruite (white) surrounded by andradite (dark and taenite–awaruite–andradite intergrowth. Arsenide composition and awaruite identification are from electron microprobe analyses of this sample. JCA 03, central zone, 1000×.

D. Andradite outlining awaruite and taenite phase-grain boundaries. Awaruite is much more abundant than taenite in this photo. (See also H.) JCA 10, outer zone, 1500×.

PLATE 1

E. Intergrown awaruite and serpentine (dark). JMS 4, 1500×.



F. Native copper (striated and mottled appearance), awaruite (evenly toned irregular grains) outlined by serpentine (dark) present along grain boundaries. Gentle etching has revealed copper deformational (?) twinning. JCA 25, 1000×.

G. Euhedral diopside crystals (darker) in andradite. JCA 01, 1000×.

H. Taenite crystal containing oriented andradite lamellae rimed by solid awaruite. Matrix is an awaruite and taenite mixture having andradite situated along phase-grain boundaries. (Compare 1D.) JMS 2, middle zone, 1500×.

geometric garnet-metal intergrowths and commonly enclose metal crystals containing fine garnet lamellae.

Two nickel-iron metal phases were found by stepwise electron microprobe traverses across the metal in a sample showing the andradite-metal intergrowth. Analysis of 28 points in the metal of this sample gave a clear bimodal distribution of nickel and iron values in alternating bands. The average composition of the metal phases was found to be 28.9 percent Fe and 68.2 percent Ni, but most of the analyses fell between 62 to 66 percent Ni and 73 to 75 percent Ni. None of the points analyzed gave results between 68.0 and 71.5 percent Ni.

The less chemically resistant phase (low nickel) was found to etch about 0.05 microns deeper than the high nickel phase after etching for one second in a solution of 5 percent $FeCl_3$ in 1:1 HCl and washing with water. Individual areas of each phase are usually a few microns across with sharp boundaries (pl. 1-B).

The more chemically resistant phase (72-75 percent Ni) is certainly the ordered phase awaruite. Its X-ray diffraction superlattice lines have been observed from each of 20 or more polished josephinite surfaces examined by scanning X-ray diffractometry. The less resistant phase (61-68 percent Ni) is presumably the disordered, high-temperature phase of the nickel-iron system, taenite. These analyses fell well outside the stability limits determined for $FeNi_3$ (73-79 percent Ni at 400°C; Viting, 1957). No ordered phase with the approximate composition $FeNi_2$ is known, and only one set of X-ray diffraction superlattice lines (those for awaruite) are observed in the two-phase metal areas. Where single-phase metal areas occur in josephinite, the metal is awaruite.

A study of the distribution and textures of taenite and awaruite in 30 josephinite specimens revealed the following regularities:

A. Where geometric intergrowth patterns of andradite occur in metal, the metal consists of two phases. Taenite and awaruite are about equally abundant in these areas. Taenite-awaruite phase boundaries among the metal-andradite intergrowths contain no precipitates to outline them. They can only be seen by etching. Taenite-awaruite phase boundaries cross cut the crystallographically oriented garnet-metal intergrowths in a random fashion. The orderly garnet lamellar pattern appears to be superimposed on a jig-saw puzzle arrangement of the two metal phases (pl. 1-B). True metal-metal grain boundaries outlined by silicates are difficult to find in areas containing the geometric garnet-metal intergrowths. Grain boundaries between what appear to be crystallographically coherent domains are much farther apart than the taenite-awaruite phase boundaries.

B. In specimens that contain awaruite alone (no taenite), the metal is only very rarely intergrown with silicates or magnetite. The awaruite crystals are relatively inclusion-free and show no internal phase boundaries after etching. The boundaries of individual crystals are easily seen because they are outlined by minerals that occur between them. Individual awaruite crystals are a few microns to a few tens of microns across in specimens of this type. Their boundaries are usually ragged and irregular, but straight-sided crystals also occur in some specimens.

C. Awaruite occurs alone in veins that penetrate the two-phase metal areas from the outside of the specimen and as crystals within and just under the serpentine skin. It appears to be paragenetically later than the two-phase metal. Awaruite, occurring as solid single-phase metal areas within the two-phase metal plus silicate intergrowths, often rims and includes nickel-iron arsenide and sulfide grains, which it has partially replaced (pl. 1-C).

D. A few specimens display intimately associated andradite and/or serpentine with a two-phase metal. However, the usually geometric intergrowths are poorly developed or missing entirely. In these cases the phase boundaries are often outlined by silicate inclusions, and they appear to be grain boundaries as well (pl. 1-D).

Serpentine and magnetite.—Josephinite specimens consisting of andradite, taenite, and awaruite almost completely lack serpentine except in their outer zones. They also contain little or no magnetite. Many specimens composed of very fine serpentine intergrowth with awaruite and taenite contain little or no andradite. The appearance of the intergrowth texture is very similar to that displayed by the metal-andradite specimens. Specimens containing metal-serpentine intergrowths also contain rectilinear magnetite intergrowths with metal. Josephinites sometime have a central zone of metal-andradite intergrowths, excluding serpentine, surrounded by intergrowths of metal, serpentine, and magnetite containing only a little garnet. Often the serpentine-metal intergrowths look loosely woven, more dendritic, grading into isolated euhedral metal crystals in a serpentine matrix (pl. 1-E). The metal intergrowth with serpentine is predominantly awaruite but contains up to about 20 percent taenite. The authors have one such specimen which appears to have been fractured, the radiating cracks later filled with solid awaruite. The class of specimens described in (D) above contains approximately equal amounts of andradite, magnetite, and serpentine with a two-phase metal in which awaruite predominates.

Specimens that contain awaruite alone also contain large amounts of closely associated serpentine and magnetite. They may also contain some andradite, but geometric metal-silicate intergrowths are rare in them. Individual awaruite crystals surrounded by serpentine often give the specimen surface a reticulated or net-textured appearance. The mineral assemblage in the outermost zone of many samples is magnetite, serpentine, and awaruite.

Serpentine also occurs as numerous veins penetrating specimens from the outside. Long, bladed, and fibrous clinochrysotile crystals occur in the veins, whereas the skin is predominantly massive antigorite, stained red-brown on the outside but becoming light, translucent green close to the metal interior. The serpentine skin contains abundant magnetite with massive magnetite forming the outer surface of the specimens in spots.

Magnetite intergrown with awaruite, native copper, and serpentine in one specimen was found to contain less than 0.01 percent Ni, Co, and Cu by electron microprobe analysis. The efficient partitioning of these elements between the native metals and magnetite in josephinite is considered to be good evidence for the maintenance of chemical equilibrium during the formation of this assemblage. Oxides of nickel and copper would not be expected to form in equilibrium with reduced iron.

Other native metals.—Native copper very rarely occurs in specimens consisting only of andradite, taenite, and awaruite but is a common constituent in samples where awaruite is the dominant or only other metal phase present. It occurs as irregular patches with awaruite, magnetite and serpentine in specimens that may or may not contain andradite (pl. 1-F). Copper in this association evidently formed syngenetically with the nickel-iron. Native copper in josephinite was found by Ramdohr (1967) to contain 0.25 to 0.5 percent nickel in solid solution. Native copper in iron meteorites contains similar amounts of dissolved nickel, but appreciable nickel has not been found in terrestrial native copper from other localities (Buseck, Holdsworth, and Scott, 1973). Mossy flakes of native copper commonly populate serpentine veins or line their borders with the nickel-iron. Copper sometimes coats exposed metal on the outside of josephinite pebbles. This copper has probably replaced nickel-iron.

Wairauite (CoFe), which was first found associated with awaruite in serpentinites from South Island, New Zealand (Challis and Long, 1964), was recently discovered in josephinite by Dick (1974). The authors have one specimen in which this alloy occurs with taenite and awaruite. Wairauite is stable to 730°C (Torok, 1973). Its association with the taenite, therefore, is a reasonable one.

Native silver was found associated with copper in a serpentine vein by Dick (1974). Native gold has also been found in several specimens.

Arsenides and sulfides.—Nickel arsenide minerals occur commonly in josephinite. They are most prevalent in specimens consisting of andradite and two-phase metal, sometimes composing more than two percent of the specimen. A pink, anisotropic arsenide with the approximate formula $(Ni,Fe)_{2-3}As$ with $Ni:Fe \approx 10:1$ was found in one such specimen. This may be the same arsenide identified by Ramdohr (1967) as orcelite (Ni_2As, formula doubtful) or a new mineral.

Oregonite $[(Ni,Fe)_2As]$ occurs in the josephinite-bearing placers of Josephine Creek but so far has not been found in josephinite. Nickel-iron arsenide minerals having metal/arsenic ratios greater than niccolite (the orthomagmatic nickel arsenide of peridotites) are associated with serpentinites and believed to be formed during serpentinization (Ramdohr, 1967).

Sulfides are much more common in specimens containing awaruite metal alone. Ramdohr (1950) has identified a number of them, including pyrrhotite, heazlewoodite, chalcopyrite, chalcocite, sphalerite, and several unknown minerals.

Other silicates.—The authors have found diopside to be the most common silicate mineral in josephinite, following andradite and serpentine. It occurs as long, bladed, euhedral crystals within the garnet and nickel-iron metal (pl. 1-G). In many specimens, aggregates of diopside crystals form veins that are gradually replaced by bladed serpentine pseudomorphs (probably clinochrysotile) toward the outside edge of the specimens they penetrate.

An electron microprobe analysis of diopside *in situ* is given in table 3. The analysis is an average of 18 analyzed grains in a single josephinite specimen. A more stoichiometric diopside is obtained if all the iron is assumed to be ferric. The wide range of color observed for this mineral (colorless–green–red brown) is probably because of its low, but extremely variable, iron content.

Electron microprobe results have suggested the presence of magnesian kirschsteinite [$Ca(Fe,Mg)SiO_4$] associated with the diopside and andradite in one josephinite specimen. More analyses and a structural determination are needed to confirm this, however.

Zonation.—Many specimens contain two or more of the above mineral assemblages arranged in roughly concentric zones. The following is given as a list of the observed zonal arrangements from innermost to outermost; it also constitutes a summary of the most common mineral assemblages encountered in josephinite.

1. Taenite and awaruite in approximately equal abundance;
   Andradite and accessory diopside;
   Minor arsenides, sulfides rare;
   Serpentine and magnetite rare or absent;
   Well developed geometric metal-andradite intergrowth texture (pl. 1-A, B).
2. Awaruite more abundant than taenite;
   Serpentine, andradite, and magnetite;
   Accessory diopside;
   Minor arsenides more abundant than sulfides;
   Geometric intergrowth absent or poorly developed;
   Silicate precipitates along awaruite-taenite phase boundaries (pl. 1-D, H, matrix).
3. Awaruite much more abundant than taenite;
   Serpentine and magnetite, accessory andradite;
   Minor arsenides, sulfides;
   Geometric/dendritic-type serpentine-metal intergrowth texture (pl. 1-E).
4. Awaruite ± trace of taenite ± native copper;
   Serpentine, magnetite, accessory andradite, diopside;
   Minor sulfides, arsenides;
   No geometric intergrowths.

5. Awaruite, native copper common and may constitute up to 30 percent of specimen;
   Serpentine and magnetite;
   Andradite usually absent;
   Sulfides predominate over arsenides;
   No geometric metal-silicate intergrowth (pl. 1-F).
6. Serpentine skin with accessory magnetite, awaruite, native copper;
   Occasionally massive magnetite.

Zones 2 and 3 have not been observed in the same specimen. Their relative order is, therefore, uncertain. There is often a boundary line of massive awaruite and taenite between zone 1 and any outlying zone.

Josephinite "in place".—The authors have acquired several serpentinite specimens that contain nickel-iron and were collected in the source locality for josephinite discovered by Dick (1974). One specimen contains a 3 mm orbicular nodule, half of which is awaruite, and half magnetite and serpentine. The matrix is massive serpentine, containing no primary minerals. The shape of this tiny nodule resembles the shape of much larger josephinite stream pebbles.

A portion of the sample showing a contact between relatively unaltered harzburgite and serpentine, described by Dick (1974) and supplied by him, was also examined by the authors. The sub-millimeter-sized metallic grains in this specimen were found to contain two-phase metal as well as a small amount of andradite. Rational intergrowth development was seen in one grain. The textural similarity between the metal-andradite intergrowths in a matrix grain and those in the josephinite stream pebbles has already been pointed out by Dick.

JOSEPHINITE CHEMICAL CHARACTERIZATION

Methods.—Josephinite was analyzed for major, minor, and trace elements using spark source mass spectrometry, neutron activation analysis, and atomic spectroscopy. Nine specimens, representing each of the mineral assemblages and textures listed above, were selected for analysis. The most thorough analysis was performed on a large metal-andradite specimen (JCE2) displaying the mineral assemblage and textures typical of this abundant and unusual type of josephinite. The specimen was carefully examined in the microscope and searched with an electron microprobe. The outermost part of the specimen contained serpentine and magnetite, but the interior, which comprised about 80 percent of the 3 to 4 ounce specimen, was found to consist only of the two-phase metal and andradite with a minor ($<$ 1 percent) amount of the nickel-iron arsenide previously described. The metal and garnet intergrowth pattern is very well developed in this specimen.

Electron microprobe analysis of the metal and garnet *in situ* was performed at the National Bureau of Standards. The nickel and iron analysis previously mentioned (table 1, second column) is an average of 28 analyzed points and is the basis for the data presented in figure 1. The metal is approximately 60 percent taenite (average composition 64.6 percent Ni)

TABLE 1

Composition of josephinite and awaruite

Element	Josephinite	Josephinite metal phase*	Awaruite	Method**
Major elements, wt %				
Ni	62.1	68.2	70.4	AA, EMP
Fe	26.7	28.9	26.2	AA, EMP
Cu	0.511	0.562	0.432	AA, INAA
As	0.292	0.26	25 ppm	INAA
Co	0.22	0.26	1.55	INAA
C	0.08	—	—	COMB.
S	0.049	0.041	0.38	SSMS
SiO_2	4.77	—	—	AA
CaO	3.21	0.21	0.02	FE
MgO	1.09	<0.02	1.03	AA
Al_2O_3	0.147	0.0081	0.129	INAA
	99.17***	98.44***	100.14	
Trace elements, ppm				
Na	112	25	71	INAA
K	13	—	450	SSMS, INAA
Sc	<0.001	—	0.64	INAA
Ti	<10	<10	79	INAA, SSMS
V	1.2	<0.1	14.2	INAA, SSMS
Cr	4.5	3.7	230	SSMS
Mn	27.7	13.2	100	INAA
Zn	≤ 1.2	—	58	SSMS
Ga	<0.2	—	3.5	SSMS
Pd	10.8	11	1.24	RNAA, SSMS
Sb	7.15	7.3	<0.2	INAA, SSMS
Ir	<0.01	—	0.12	RNAA
Pt	0.086	—	1.34	RNAA
Au	0.95	—	3.3	RNAA
Pb	0.20	—	10	SSMS

Elements not detected in josephinite and awaruite

Detection limit, ppm	Element
1	Sr, Ba
0.1	Se, Rb, Cd,**** Hf, Ta, Zr, Th, U, W, Os, Ru, La, Ce, Nd, Pr, Gd, Tb, Ho, Er, Tm, Yb
0.01	Be****
0.001	Lu, Sm, Eu, Dy

* Metal phase separate includes the minor arsenide. See text.

** AA—atomic absorption, INAA—instrumental neutron activation analysis, COMB—Leco direct combustion analysis, SSMS—spark source mass spectrometry, RNAA—radio-chemical neutron activation analysis, FE—flame emission spectrometry, EMP—electron microprobe analysis.

*** Total major element composition for josephinite does not include oxygen combined with Fe and Ni.

**** Not determined in awaruite.

and 40 percent awaruite (average composition 72.9 percent Ni). The total range of nickel analysis observed was 60.8 to 74.6 percent, and the range of iron analysis was 22.2 to 35.2 percent.

Electron microprobe analysis of the andradite is given in table 2. The garnet was found to be homogeneous, and the microprobe data given are an average of 11 analyzed points, each in a different grain. The standards used were: pure elements for Si, Al, Fe, and Mg; Garnet 110752 USNM for Ca. A calculation of the number of ions in the fourfold, sixfold, and eightfold coordinated garnet sites shows that nearly stoichiometric andradite is obtained if all the iron is assumed to be present as Fe(III). An attempt was made to determine the Fe(II)/Fe(III) ratio in the garnet using the method developed by Albee and Chodos (1970). The Fe $L\beta/L\alpha$ line intensity ratios for the josephinite garnet and nine silicate standards having known Fe(II)/Fe(III) ratios were measured. The Fe $L\beta/L\alpha$ ratios obtained for the josephinite andradite were found to be indistinguishable from those obtained for two andradite standards (100 percent Fe(III)) within the margin of error produced by scatter in the data points obtained.

The complete bulk analysis of the interior portion of this specimen is listed in table 1, column 1. The specimen consists of approximately 86 percent metal and 14 percent andradite by weight ($\rho = 7.02$ g/cc). Our analysis of awaruite metal from its type locality at Awarua Bay, New Zealand, is also presented in table 1. Bright shiny grains of this mineral were separated by handpicking from a sample of black sand.

A portion of the above josephinite sample, after the exterior zone had been removed, was ground to a fine homogeneous powder. Subsamples of this were used for neutron activation analysis and atomic spectroscopy. Electrodes for spark source mass spectrometry consisting of metal and garnet fine enough to be homogeneously distributed were cut from the specimen and used without further treatment, taking advantage of the conducting nature of this material. A set of NBS microchemically homogeneous steels 661 to 665 was used for standardization. The specimen was homogeneous enough to allow a precision of 20 percent relative standard deviation (RSD) to be obtained for 3 to 5 mass spectrometric determinations of most elements. Electrodes prepared from powdered and homogenized samples mixed with In and Re doped graphite were used to determine inhomogeneously distributed elements. Because of their small size (< 2 mm), the awaruite grains had to be pelletized to form electrodes.

The precision obtained in atomic absorption and flame emission spectrometry for 2 to 3 determinations of each element was better than 4 percent RSD. Nickel and iron were most precisely determined at about 1 percent.

Neutron activation results for josephinite and awaruite are based on two determinations for each element. The precision obtained for josephinite is better than 10 percent RSD for all but two elements. The RSD for Au was 13 percent, and that for Pd was 23 percent. Awaruite determinations are somewhat less precise due to sample inhomogeneity.

Many elements in josephinite and awaruite were determined by two methods. For these, either the average of both methods or the results from the most reliable method is reported.

Solid metal and andradite were chemically separated from a subsample of the same powder used for the bulk analysis. A minor and trace element analysis of the metal separate is given in table 1, column 2. The andradite analysis is given in table 2.

An excellent separation of andradite from metal was obtained, as evidenced by its low nickel content (240 ppm). The metal separate includes the minor arsenide mineral and silicate components totaling less than 1 percent. Similar amounts of Mg, Si, and Ca (0.05-0.2 percent) were reported in the metal phase as a result of the electron microprobe study. Their detection and measurement were complicated by line interferences, however. At this point, it is impossible to tell whether the minor amounts of Ca, Mg, and Al found in the metal separate are dissolved in the metal phase or are due to less than 1 percent unseparated andradite. The latter possibility is more likely in view of the similar Ca/Al ratio exhibited by the metal separate and the analyzed andradite.

A suite of josephinite specimens exhibiting the various mineral assemblages and textures discussed above was analyzed for selected elements, and the results appear in table 4. In the case of zoned specimens one particular zone was selected for analysis. Electron microprobe analyses of the metals in these specimens were also performed.

Results.—Josephinites are at least as diverse chemically as they are mineralogically and are usually heterogeneous on a microscale. Many elements, in addition to being distributed among the major phases in josephinite, concentrate in minor phases of their own. As, S, Cu, Au, Ag, Co, and probably Pb, Zn, Cr, and C form minor minerals of common to sporadic occurrences in a collection of specimens. Minor elements contained in minor phases will become trace elements in the bulk analysis of a rock or separated mineral including that phase. These may be difficult to distinguish from trace elements homogeneously distributed in a major phase.

An attempt to unravel the complexities of the elemental distributions among the major and minor phases in josephinite involved the use of light microscopy, bulk analysis (to determine what elements are present at all levels), electron microprobe analysis, and the analysis of chemically separated minerals. In addition, a heterogeneity study, based on spark source mass spectrometric photoplate results from neat, unhomogenized samples, was used to determine what elements are concentrated in minor and trace minerals not observed in the microscope. The ion imaging mass analyzer provided ion images of several elements from a single area. Superimposing these images yielded qualitative information on elements concentrated in minor phases. Attempts to correlate the abundance of trace elements with the abundance of a minor phase in several specimens helped to further resolve ambiguities.

Thorough characterization of a relatively simple sample (JCE2 described above: taenite, awaruite, andradite, minor nickel-iron arsenide) provided an important data base for further study. A comparison of the abundances of elements in the bulk analysis and separated metal (table 1) with the separated andradite analysis (table 2) will reveal which elements are primarily in the metal (plus arsenide), which are in the garnet, and which are distributed between the two components. Of the minor elements, Cu, Co, and S are homogeneously distributed (dissolved) in the metal. The minor arsenide was analyzed by electron microprobe and found to contain only Ni, Fe, and As above the level of a few tenths of 1 percent. It cannot, therefore, account for any appreciable amount of these elements.

Taenite, awaruite, and wairauite intimately associated in one josephinite were analyzed for Ni, Fe, and Co by electron microprobe. The taenite (avg composition 64.8 percent Ni) and the awaruite (avg composition 74.3 percent Ni) each contained about 0.6 percent Co while the wairauite contained about the same amount of dissolved nickel. It is reasonable, then, to suspect the presence of wairauite in a josephinite or awaruite sample containing greater than about 0.6 percent Co. The metal

TABLE 2

Analysis of andradite in josephinite

Major elements as oxides	Weight %*	Element	Numbers of ions on basis of 24 oxygens**
SiO_2	35.8 ± 0.1	Si	6.05
Fe_2O_3	29.7 ± 0.3	Fe	3.86
Al_2O_3	0.5 ± 0.1	Al	
CaO	33.0 ± 0.2	Ca	6.03
MgO	0.3 ± 0.1	Mg	
Total	99.3		

Minor and trace elements†

Element	Concentration, ppm
Ni	240
Mn	86
Cr	27
Ti	9.6
P	3.9
Co	1.9
Cu	1.5
W, V, Pb, Mo	0.4-0.8
Li	0.054
Na	(20)

Element	Upper limit concentration,‡ ppm
K, Y, Sr	1.0 -0.5
Sn, Zr, Ba, Nb, Rb	0.25-0.1
Ce, La, Cd, Cs, Be	0.06-0.01

Elements not detected	Detection limit, ppm
REE except Ce and La Hf, Th, U	0.005

* Electron microprobe analysis. All Fe calculated as Fe_2O_3.

** Pure andradite yields Si = 6, Fe = 4, and Ca = 6.

† Spark source mass spectrometric analysis.

‡ Spectral lines may include interferences at these low levels—only upper limits are given.

separate analyzed for table 1 (0.26 percent Co) probably contains none. The copper content of awaruite associated with native copper may be as high as 5 percent. The native copper in this association may contain up to 5 percent nickel and up to 1 percent each of iron and cobalt. Cobalt probably substitutes primarily for iron, and copper for nickel in the awaruite lattice. Most of the arsenic is present as the nickel-iron arsenide. The arsenic concentration in the metal has not yet been determined but probably does not greatly exceed that of sulfur (0.04 percent). An arsenide phase was seen in a josephinite specimen containing only 1200 ppm As.

Of the trace elements, Pd, Sb, Te, and Bi were found to occupy the metal separate almost exclusively. Te and Bi bulk values agreed reasonably well with the metal values, and they appear in table 4. Mn, Cr, and Mo are distributed between the metal and garnet but favor the garnet. The Mo concentration in the metal (4.5 ppm) is greater than 10 times its concentration in the garnet (0.4 ppm). Au and Ag were found in the metal separate but are extremely inhomogeneously distributed. They probably occur in this sample as trace native metals.

It is more difficult to determine whether Pd, Sb, Te, and Bi are dissolved in the arsenide or dissolved in the metal. If they were present in the arsenide only, concentrations of each element close to 0.1 percent would be required. Their abundance, in samples of similar mineralogy, should exhibit a good correlation with the arsenic (arsenide) abundance in the specimens. The correlations between these elements and arsenic in four similar josephinite specimens (table 4, JCA03-JMS5) were found to be rather poor over a range of arsenic values of 1800 to 7000 ppm. Pd and Te display a good correlation with each other, however. Ion images of Pd, Sb, and Te of a josephinite surface area were completely different from an arsenic image of the same area. The arsenic image showed spotty concentrations of this element, the Pd, Sb, and Te images, a homogeneous haze. The authors conclude, therefore, that Pd, Sb, Te, and Bi are dominantly dissolved in the metal.

TABLE 3

Analysis of diopside in josephinite

Oxides	Weight %*	Element	Number of ions on basis of 24 oxygens**
SiO_2	52.3 ± 0.8	Si	8.00
Al_2O_3	0.2	Al	
Fe_2O_3	1.7 ± 1.2	Fe	
MgO	17.9 ± 0.5	Mg	4.02
MnO	0.01	Mn	
NiO	0.3	Ni	
CaO	25.6 ± 0.7	Ca	4.08
Total	98.0†		

* Electron microprobe analysis. All iron computed as Fe_2O_3.

** Pure diopside yields: Si = 8, Mg = 4, Ca = 4.

† Low total may be due to the presence of elements not determined: Ti, Na, K, Cr, et cetera.

TABLE 4

Josephinite: paragenetic-chemical sequence

Sample	Metal* Ni/Fe	Mg/Ca	As/S	Cu%	Ag	Pd	Sb	Te	Bi	Zn	Pb	Model formation temp interval	Chemical environment classification	Mineral assemblage** and texture
JCA 03 Central zone	2.82	0.094	14	0.32	0.05	13	17	13	0.60	0.94	1.5	500°-450°C	Arsenic-calcium regime	Tae., Aw., And., minor Ars. rational intergrowth well developed (zone 1).
JCE 2 Central zone	2.42	0.29	6.0	0.51	0.34	11	7.2	11	3.3	1.2	0.2			Same (zone 1).
JMS 2 Central zone	2.50	0.60	4.4	0.26	0.20	22	17	32	5.2	0.60	1.9			Same + minor serpentine less well developed intergrowth (zone 1).
JMS 5 Central zone	2.55	68	2.6	0.17	0.34	12	12	10	3.6	3.1	1.7	450°-375°C	Transitional	2 ϕ metal, Serp., trace Mgt., Ars., Sulfs., little rational intergrowth Serp., on ϕ boundaries (zone 2).
JCA 14	2.78	0.78	0.75	0.10	0.14	7.0	3.7	3.8	2.4	0.80	1.0			Aw., minor Tae., and Mgt., Serp. (bladed and massive). Minor diopside, Sulfs., Ars. No rational intergrowth (zone 4).
JMS 4	3.10	160	1.6	0.081	0.14	1.3	3.4	14	1.3	1.0	1.0			Aw., minor Tae., Serp. rational dendritic intergrowth texture (zone 3).

JCA 04	3.13	0.37	0.31	5.7	17	3.0	<1	≤4.1‡	1.2	3.2	29			Aw., And., Mgt., Cu., Serp., minor CoFe, Tac., Sulfs. No rational intergrowth (zone 4).
JCA 25	3.04	23	0.29	24.1	42	<0.2	<1	≤8.0‡	3.2	57	1.1	below 375 °C	Sulfur-magnesium regime	Aw., Cu., 2 Serp., Mgt., minor Sulfs. (zone 5). No rational intergrowth, minor dendrite formation.
JMS 1	2.95	42	0.33	22.5	43	0.28	<1	≤14‡	1.2	44	2.3			Aw., Cu., Serp., Mgt., minor Sulfs. No patterned intergrowths (zone 5).
Awaruite	3.26†	44	0.0066	0.43	<1	1.2	<0.2	<3	<1	58	10			<2 mm diameter grains minor included Serp., Sulfs. No patterned intergrowths.

* Separated nickel-iron metal. Co subtracted as CoFe. Other results from bulk analyses. Ni, Fe, Mg, Ca-FE. As, Cu-INAA. Remainder-SSMS.

**Tae. = taenite; Aw. = awaruite; And. = andradite; Serp. = serpentine; Mgt. = magnetite; Ars. = arsenides; Sulfs. = sulfides; Cu. = native copper.

† Average of 11 analyses compiled from the literature. Pure $FeNi_3$ = 3.15.

‡ Spectral interference from Cu_2^+ ions allows only an upper limit to be given.

The andradite has several notable peculiarities. Although Ni has been found to enter the garnet structure (Geller, 1967), its concentration in the andradite of josephinite is very low. The nickel abundance in andradite approaches the abundance of nickel in the olivine of pallasites (40-150 ppm) (Moore, 1971). The very low Ni^{++}/Ni° ratio in josephinite probably reflects the strongly reducing conditions under which the material formed. The andradite is very pure, of nearly the end member composition, and homogeneous with respect to major and trace elements.

It is also very unusual when compared with other garnets because of its extreme depletion in trace lithophile elements such as the rare earth elements, Y, Sr, Ba, Zr, Nb, Hf, Th, U, and Ti. The low abundance of Ti, Sr, Y, Nb, and the heavy rare earth elements in this andradite is particularly surprising because andradite and other garnets are known to have relatively large concentrations of these elements (Jaffe, 1951).

A chemical comparison can be made between the New Zealand awaruite and the metal of josephinite using the data from tables 1 and 4. The average Ni/Fe ratio in the metal of three josephinite specimens having geometric metal-andradite intergrowths is 2.38 compared to 2.69 for the New Zealand awaruite. The average Ni/Fe ratio for 11 analyzed awaruite samples compiled from the literature is 3.06 ± 0.41. This is probably a more representative value for the Ni/Fe ratio in awaruite, as pure $FeNi_3$ yields a Ni/Fe ratio of 3.15. The effect of Co present with awaruite as CoFe would be to lower the determined Ni/Fe ratio below the actual value for the awaruite in that sample. Calculating all the Co in the New Zealand awaruite as CoFe, for example, yields a Ni/Fe ratio of 2.85 for the awaruite. The Ni/Fe ratios shown in table 4 have been corrected in this manner. Ratios between about 2.70 and 4.00 are possible within the stability field determined for synthetic awaruite at 400°C (Viting, 1957). The lower Ni/Fe ratios determined for the josephinite metal are due to the presence of taenite in these samples.

More dramatic differences are found between the abundances of minor and trace elements in the josephinite metal and their abundances in awaruite. Sb, Te, and Bi, which are present in the josephinite metal in easily measurable quantities, were not detected in awaruite. The abundances of elements having chalcophile affinities such as Zn, V, Mn, Pb, and S are much greater in awaruite than in josephinite. The Pd/Pt ratio of 126 determined for josephinite (bulk analysis) is in sharp contrast to that determined for awaruite (0.93). The Pd/Pt ratio in awaruite is within a factor of 10 of many sulfide bearing ore bodies of mafic and ultramafic rocks yielding precious metals (Parthe and Crocket, 1972). Iridium was measurable in awaruite (0.12 ppm) but not in josephinite ($<$ 0.01 ppm). Considerable differences also exist between the abundances of As, K, Sc, Ti, Cr, and Ga in josephinite and awaruite; however, these elements are much less likely to be present primarily in the metal of either material. Their abundances reflect the different chemistry of the associated minor minerals in each case.

The results of electron microprobe analyses of the metal phases in the josephinites chosen for table 4 confirmed their metallographic identification and provided information on their composition. The compositions of coexisting taenite and awaruite are especially important. They are related to temperature of formation by the iron-nickel binary phase diagram (Goldstein, 1973).

The distribution of nickel analyses found by probe in the large andradite-metal geometric intergrowth specimen (JCE2) is plotted beneath a portion of the phase diagram in figure 1. Fifty metal analyses for each of two additional andradite-metal intergrowth specimens (JCA03, JCA01) generated bimodal distributions of nickel and iron results very similar to that shown in figure 1. In contrast, traverses searching specimen JCA25 failed to discover a single grain of taenite. Thirty-one analyzed points yielded nickel values between 72 and 75 percent with an average Ni/Fe ratio of 3.14; pure $FeNi_3$ yields 3.15. The major portion of specimen JCA04 is metallographically and texturally similar to JCA25, but a small, central, taenite bearing zone is also present. Twenty-eight analyzed points in the large outer zone revealed only awaruite (73-76 percent Ni, Ni/Fe ratio 3.20). Taenite associated with awaruite and wairauite in the central zone was found to contain only 58 to 63 percent Ni. According to the iron-nickel binary phase diagram, an alloy of this composition would coexist in equilibrium with awaruite at temperatures of about 400° to 430°C. This central zone shows no geometric andradite-metal intergrowth, although andradite is present in abundance. The relatively iron-rich taenite is just what would be expected to be present in the center of a specimen formed at temperatures predominantly below the lower stability limit of taenite (about 350°C), if the outer zone was added to a nucleus formed at higher temperature.

The nine josephinite specimens analyzed for table 4 display a wide range of abundances for the minor and trace elements. The abundances of the trace elements (particularly Pd and Sb), present in the metal of josephinite, do not vary randomly among the various mineral assemblages and textural types but decline smoothly from zone 1 to zone 5 type assemblages. The abundances of As, S, Zn, and Pb, present in minor minerals in josephinite, also exhibit a correlation with the zonal sequence of petrologic types.

DISCUSSION

Josephinite mineral paragenesis.—Under the microscope, josephinite specimens at first appear to be very different from one another. It is impossible to predict what mineral assemblages will be found inside a specimen before it is cut open and polished. They each contain a treasure chest of rare minerals and a Pandora's box of complex and confusing textures. However, with confidence developed from finding consistencies in a large number of specimens, the authors believe it is possible to establish the paragenesis of the various minerals and mineral assemblages in josephinite.

The observation that josephinite specimens display a number of different mineral assemblages, and that two or more of these often occur in a single specimen arranged in roughly concentric zones, suggests that individual specimens probably formed over a range of temperatures and chemical conditions. An attempt can then be made to sort out the various mineral assemblages and their relative temperatures of formation. The assumption is made that the mineral associations are at equilibrium at the temperatures at which they formed. The authors hold the view that individual josephinite specimens probably "grew" or that material was added to a nucleus of one particular mineral assemblage over a range of temperatures. All the minerals, then, are secondary or redeposited. An alternate view holds that josephinite specimens originally consisted entirely of one primary (high temperature) mineral assemblage which was subsequently altered at lower temperatures, undergoing a form of retrograde metamorphism to produce the present variety of mineral associations observed. Petrographic observations are often ambiguous, but the wide range of abundances in josephinite for trace elements present in the metal is not what would be expected if the lower temperature mineral assemblages are the result of alteration of an original high temperature assemblage. The metal itself must be assumed to be original. It should retain a semblance of its original trace element composition even after phase changes and partial oxidation accompanying replacement.

Clues to the order of formation of the mineral assemblages can be found from a study of the zoning and cross-cutting relationships exhibited in the specimens.

An estimate of the temperature of formation of these assemblages can be derived from a study of the composition and distribution of taenite and awaruite among them, with reference to the iron-nickel binary phase diagram (Goldstein, 1973).

The assemblage of andradite intergrown with taenite and awaruite, which forms the central zone of many specimens, is probably the earliest surviving mineral assemblage in josephinite. Reference to the iron-nickel binary phase diagram will show that taenite and awaruite coexist within a two-phase region between 500° and about 350°C. Taenite compositions between 60 and 76 percent Ni upon cooling from higher temperatures will break down into the two-phase taenite-awaruite assemblage between 500° (76 percent Ni) and 400°C (60 percent Ni). Nickel-iron metal having the bulk composition of 68 percent Ni (specimen analyzed for table 1) would be stable as taenite above about 460°C and as a two-phase assemblage of taenite and awaruite between 460° and 350°C. The andradite-metal intergrowth exhibited by this specimen, if formed above 460°C, may have developed the two-phase metal upon cooling below this temperature. Alternately, the geometric metal-andradite intergrowth may have formed between 460° and 350°C where taenite and awaruite are stable together.

If the andradite-metal intergrowth is postulated to have formed within the two-phase region, temperatures right up to 460°C would be required to generate the distribution of nickel analyses shown in figure 1. The authors are convinced that josephinite specimens showing the geometric andradite-two phase metal intergrowths formed at temperatures above the taenite-awaruite-two-phase region. The data presented in figure 1 are given as evidence that the metal of this specimen cooled through the interval of 460° to about 400°C. The following additional evidence must be considered:

1. Metal-metal phase boundaries are terminated against the orderly garnet-metal intergrowth patterns in a random way (pl. 1-B). The development of the two coexisting metal phases, then, is probably later than the establishment of the garnet intergrowth in the metal. The rectilinear intergrowth pattern would seem more likely to form with the help of crystallographic control exerted by its development within a single phase alloy. By slowly cooling a synthetic alloy of the composition 70.2 atomic

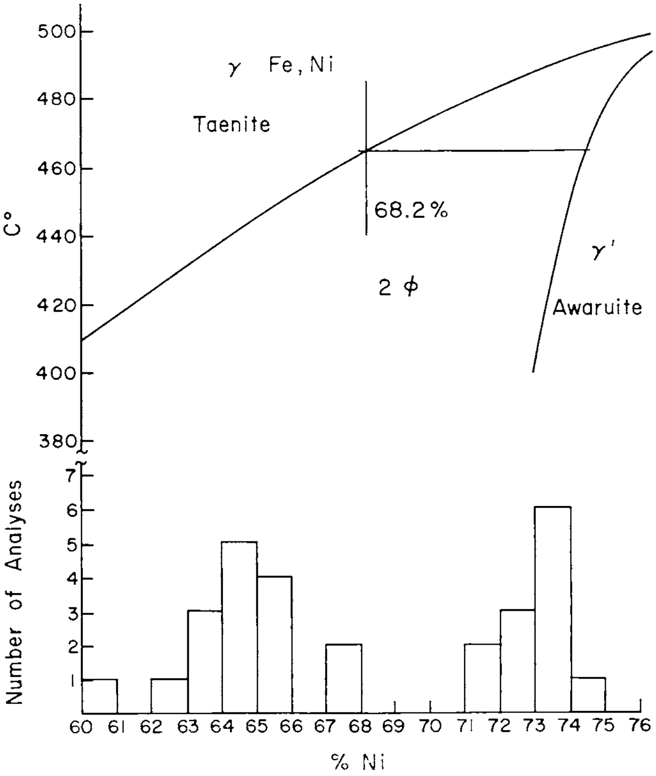


Fig. 1. Distribution of electron microprobe analyses of the metal in josephinite JCE 2 plotted beneath a portion of the iron–nickel binary phase diagram. Bulk composition of the metal equals 68.2 wt percent Ni. Phase diagram data from Goldstein, 1973.

percent Ni and 29.8 atomic percent iron through the interval 490° to 400°C, Viting (1957) was able to produce a two-phase metal showing a pattern of taenite-awaruite phase boundaries very similar to that observed in josephinite.

2. Silicate precipitates are generally not found between metal-metal phase boundaries interwoven with the rectilinear garnet lamellae. In areas where silicates do occur along the taenite-awaruite phase boundaries, the patterned intergrowths have not developed.

3. In one specimen, single euhedral taenite crystals contain intergrown garnet in their cores but have a rim of solid awaruite. These are completely surrounded by two-phase metal and garnet, showing no rectilinear intergrowth (pl. 1-H).

Specimen areas consisting of awaruite and taenite with other minerals trapped along the phase boundaries and showing little or no development of the rectilinear intergrowth (zone 2 above) may have formed at temperatures within the taenite-awaruite two-phase region (∽ 460°-350°C). The class of specimens described as zone 3 in which serpentine forms patterned intergrowths with a metal (which is dominantly awaruite) probably formed within this interval also. The mineral association described as zone 4 may have formed at the base of this interval, as it contains a small amount of taenite.

According to the iron-nickel binary phase diagram, at temperatures below 350°C, awaruite may form alone or in association with either αFe at the iron-rich end of the system, or nearly pure nickel. Neither αFe nor pure nickel has been found in josephinite, although αFe has been found associated with awaruite in other localities (Chamberlain and others, 1965; Ramdohr, 1967). Specimens having awaruite as the only metal phase presumably formed below about 357° to 350°C, where taenite is not stable. The breakdown of taenite formed above this temperature to αFe and awaruite at lower temperatures is predicted by the phase diagram. The fact that taenite still exists and αFe has not as yet been observed in josephinite may be an indication that this lower temperature breakdown is kinetically inhibited.

A model summarizing the sequence of formation of the various mineral assemblages with estimates of temperature and descriptions of the resulting textures is presented in figure 2. Native nickel-iron occurrences in other parts of the world consist typically of ragged, irregular, 1 to 100 micron sized grains in close association with magnetite, nickel sulfide minerals (pentlandite, heazlewoodite), and occasionally native copper in a serpentinite matrix. This association parallels the lowest temperature mineral assemblage found in josephinite. Recent estimates of the temperature of formation of awaruite-bearing mineral assemblages in serpentinized rocks have been given by Ramdohr (1967) as 250° to 300°C, Hultin (1968) as 250° to 400°C, and Chamberlain (1965) as about 350°C. Chamberlain's estimate is based on experimental decomposition of primary sulfide minerals to yield native metals (Chamberlain and others, 1965).

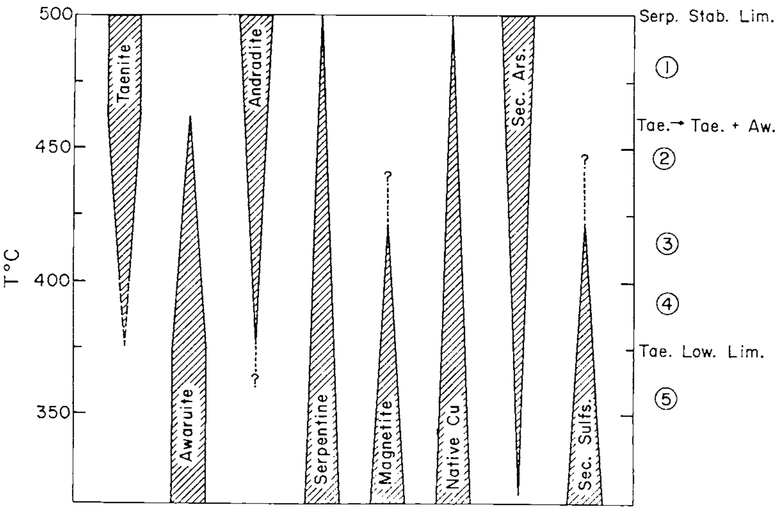


Fig. 2. Temperature of formation of assemblages of the most common minerals in josephinite. Circled numbers at right refer to zonal arrangement described in text. Assemblages are diagrammed as they presumably existed at a particular temperature. One is therefore hypothetical. (Taenite no longer exists alone in josephinite.) Sec. = secondary; Ars. = arsenides; Sulfs. = sulfides; Serp. = serpentine; Tae. = taenite; Aw. = awaruite; Stab. = stability; Lim. = limit; Low. = lower.

Geologic evidence provided by the discovery of the metal-andradite association in place in serpentinite would appear to constrain the temperature interval within which josephinite can form to the temperatures at which serpentinization can take place: temperatures beneath the upper stability limit of serpentine. Bowen and Tuttle (1949) established the upper temperature limit for the serpentinization of a harzburgite at close to 500°C. The stability limit of serpentine is rather insensitive to pressure above a few kilobars (Kitahara, Takenouchi, and Kennedy, 1966). The highest temperature mineral assemblage in josephinite probably formed above 460°C. A recent investigation (Scarfe and Wyllie, 1967) has shown that for serpentinization to occur above 460°C at least 2 kb of water pressure are required.

The evidence given above supports the conclusion that josephinite formed over a range of temperatures. Each of the mineral assemblages and textures described probably formed within a segment of this range. The suite of josephinite specimens analyzed for table 4 was selected to be representative of the important mineral assemblages and to cover the entire range of temperatures of formation of josephinite.

The analyzed mineral assemblages are arranged in the table according to their temperature of formation interval as determined using the metallographic-textural model. A description of each mineral assemblage appears at the extreme right of table 4. The first four columns are given to define quantitatively the mineral assemblage analyzed. They can be interpreted in terms of the relative amounts of the minerals present, thus: Ni/Fe in metal = awaruite/taenite, Mg/Ca = serpentine minerals/andradite, and As/S = arsenide minerals/sulfide minerals. The column Cu% shows the amounts of native copper in the bottom three josephinite specimens. The top six josephinites contain only copper dissolved in nickel-iron (no native copper). The native copper carries silver with it either in solution or as a minor associated native metal (column 5). It does not, however, contain appreciable amounts of any of the other elements listed in table 4.

A trend in the Ni/Fe ratio of the metal from lower to higher values with decreasing temperatures of formation reflects the gradual disappearance of taenite in specimens formed at lower temperatures. Specimen JCA03 has an unusually high Ni/Fe ratio compared to others in its class. It displays the usual two phase metal upon etching, although a much longer etching time is required to bring out the phase boundaries distinctly. The taenite and awaruite in this specimen are probably very close in composition. This observation is perfectly consistent, however, with an original taenite (bulk composition 73.7 percent Ni, 26.3 percent Fe) exsolving awaruite at a temperature close to 490°C. JCA03, then, is a logical choice for the top (highest temperature) entry in table 4.

The As/S ratio and the abundances of the trace elements in josephinite, particularly Pd, Sb, Te, and Zn, exhibit a marked dependence upon the temperature of formation. This observation is not easily explained in terms of physical chemical parameters dependent only on temperature.

The authors believe the observed range in composition for josephinite formed over a range in temperature can be attributed to an evolving chemical environment of serpentinization during its formation. The mineralogy and chemical composition of the New Zealand awaruite can be viewed as one end member of a temperature dependent, paragenetic-chemical sequence of metallogenetic products, formed in a chemically evolving serpentinization environment.

In summary: Josephinite probably formed over a range of temperatures from very close to the upper stability limit of serpentine (~ 500°C) to 350°C or below. This, combined with the effects of a changing chemical environment, has produced the variety of distinct mineral assemblages and textures represented in a collection of specimens. A study of the metal phases, textures, and zoning present in these specimens allowed the authors to order the various mineral assemblages according to temperature of formation. The specimens formed at the top of this temperature range, in particular, are distinctly different from any other occurrence of terrestrial native nickel iron. Specimens formed at the low end of the range bear mineral associations and textures similar to other occurrences of native nickel iron, albeit on a grand scale. It remains now to examine the environment of the origin of josephinite and the serpentinization process, to determine what factors contribute toward the formation of native metals in serpentine and what combination of these factors has resulted in the creation of the unique Josephine County nickel-iron.

Environment of origin.—Josephinite consists of minerals we believe to be secondary in origin. They were formed by the redeposition of the components of decomposed orthomagmatic minerals from the host peridotite during its serpentinization. The formation of josephinite would seem to require:

1. a source of its chemical components: Ni, Fe, Co, Cu, CaO, et cetera;
2. a reducing agent;
3. a mechanism of concentrating and transporting its components, perhaps as ions in a fluid phase;
4. a mechanism of depositing the material over a range of temperatures and chemical conditions to produce all the various mineral assemblages.

The size of josephinite specimens is ample demonstration that metals were concentrated and transported in some mobile phase over considerable distances within the serpentinizing rock. The formation of a 1 kg specimen in serpentine originally containing 2000 ppm Ni would completely remove this element from a spherical volume of rock with a diameter of about 70 cm. The serpentinites collected in the source area bear witness to a transport process themselves. Some contain networks of microscopic cracks lined with or filled by nickel-iron metal. The metal was evidently precipitated from a fluid phase moving through cracks in the serpentinite. Shearing, synchronous with the serpentinization in the source area, probably aided the movement of fluids.

Serpentinite normally contains abundant magnetite. The formation of serpentine and magnetite from the reaction of ferrous iron bearing olivine and pyroxenes with water vapor is said by several authors (Thayer, 1966; Chamberlain and others, 1965; Ramdohr, 1967) to result in the production of hydrogen gas:

$$6\ \mathrm{Mg_{1.5}Fe_{.5}SiO_4} + 7\ \mathrm{H_2O} = 3\ \mathrm{Mg_3Si_2O_5(OH)_4} + \mathrm{H_2} + \mathrm{Fe_3O_4}$$

The hydrogen thus formed is free to react with silicate nickel released by decomposing olivine (Eckstrand, 1975) or with primary sulfide minerals containing Ni, Fe, Co, and Cu (Chamberlain and others, 1965). Native metals are the result of reduction. Chamberlain and others (1965) stressed the importance of sulfide minerals in the formation of native metals in the Muskox Intrusion and in other localities (Chamberlain, 1966). In every locality thus far described, awaruite has been found in close association with primary and secondary nickel-iron sulfide minerals (pyrrhotite, pentlandite, mackinawite, and heazlewoodite). Native copper is found in association with copper sulfide minerals such as chalcopyrite and chalcocite. In some serpentinites, primary sulfides are no longer present (Hultin,

1968) but have apparently been completely reduced by reactions of the following type (Chamberlain and others, 1965):

$$\underset{\text{“pentlandite”}}{3\,FeNiS_2} + 4\,H_2 = \underset{\text{awaruite}}{FeNi_3} + \underset{\substack{\text{pyrrhotite or}\\ \text{mackinawite}}}{2\,FeS} + 4\,H_2S$$

$$\underset{\text{pyrrhotite}}{FeS} + H_2 = \underset{\text{native iron}}{Fe} + H_2$$

$$\underset{\text{chalcocite}}{Cu_2S} + H_2S = \underset{\text{native copper}}{2\,Cu} + H_2S$$

Awaruite forms the end member of a paragenetic sequence of minerals: nickeliferous pyrrhotite, pentlandite, heazlewoodite, and awaruite (Krishnarao, 1964). Each mineral has a greater Ni/S ratio than the previous one. The process producing this sequence of minerals has been called desulfurization (Chamberlain, 1967). Desulfurization of primary sulfides, driven by hydrogen production during serpentinization, results in the formation of native metals, a series of secondary sulfides, and H_2S. The H_2S is free to move through the serpentinite perhaps to be redeposited as secondary sulfides in a locality far removed from its source (Chamberlain and others, 1965). Primary nickel arsenides such as niccolite can be reduced similarly to native metals and arsine. H_2S and H_3As are thus freed and may enter a mobile fluid phase in the serpentinite together.

Perhaps the best documented hydrothermal fluid phase known to be active in serpentinizing ultramafic rocks is a Ca-rich aqueous solution to which the creation of calcium metasomatites in serpentine regions may be attributed (Barnes, Rapp, and O'Neil, 1972). This solution is believed to be reducing in nature and is capable of replacing the primary minerals of a diabase dike intruded into serpentinite with hydrogrossular, idocrase, diopside, prehnite, and xonotolite; an assemblage called "rodingite". The Ca contained in these solutions is believed to be derived from the serpentinization of Ca-bearing pyroxenes. The solution may deposit andradite as well as other Ca-rich minerals (Coleman, 1967). The authors' collection includes many samples of rodingized diabase dikes, which are abundant in the Josephine Creek area.

It is conceivable that a mobile Ca-rich aqueous solution might be formed which also carried Ni, Fe, Co, Cu, H_2S, and H_3As in solution as well as the other components of josephinite. This would simply be a solution containing elements released by minerals broken down during serpentinization. Precipitates deposited by springs of Ca-rich water issuing from serpentinite were found by Barnes, Rapp, and O'Neil (1972) to contain appreciable Ni and Fe as well as a small amount of Cu and Co. The metals in solution would be carried as oxidized ionic species if the activity of hydrogen in the solution was held low enough. This solution, upon migrating to a region where the activity of hydrogen was much higher (high H_2/H_2O ratio), would be forced to deposit native metals. Such a region might occur at the serpentinization front where the developing serpentinite shear zone is advancing into fresh harzburgite (Dick, 1974). Eckstrand (1975) envisioned water moving through serpentinite toward an advancing serpentinization front; the most strongly reducing conditions developing at the contact with unaltered ultramafic rock. This contact zone would also be an area of high Ca activity due to the decomposition of pyroxenes in progress.

Rock samples taken at the edge of the serpentine shear zone where it was in contact with unaltered harzburgite were found by Holmes Gillette and Henry Dick (private commun., 1975) to contain nickel iron and andradite intergrown on a sub-micron scale, individual grains being only on the order of a few microns across. The authors have confirmed the two-phase nature of this metal. Andradite-metal intergrowths were clearly forming right at the edge of the serpentinization front. The birth of the highest temperature mineral assemblage in josephinite can now be more clearly understood.

A solution of the metal ions and silicate components, particularly Ca, upon migrating into the serpentinization front encountered high hydrogen and Ca activity, forcing the deposition of native metals with andradite at a temperature between about 450° and 500°C. An equation for the reaction taking place in this zone can be written:

$$3\,CaMgSi_2O_6 + 9\,Mg_{\frac{5}{3}}Fe_{\frac{1}{3}}SiO_4 + 12\,H_2O \rightleftarrows$$

diopside or diopside component of pyroxenes	Fe-bearing olivine

$$6\,Mg_3SiO_2O_5(OH)_4 \quad + \quad Ca_3Fe_2Si_3O_{12} \quad + \quad Fe$$

serpentine	andradite	native iron

Nickel and other metals provided by the incoming hydrothermal solution resulted in the formation of nickel-rich taenite and other native metals rather than native iron. Josephinite so nucleated may have continued to grow as the serpentinization front slowly advanced. It would have been supplied continually with fresh metallogenic solution moving in from the main serpentinite mass. Once the serpentinization front had advanced well past a particular area the temperature as well as the hydrogen activity (ratio pH_2O/pH_2) would fall. It is in this environment that the lower temperature mineral assemblages in josephinite were probably formed.

Temperature was apparently not an important factor in determining the ultimate size of the josephinite specimens. No relationship between the size of specimens and the temperature at which they formed has been observed. Indeed, the largest specimen in the authors' collection is of the lowest temperature type (JCA25). The development of large size josephinite specimens at any temperature would have required the maintenance of a rich, freely circulating metal-bearing hydrothermal fluid for a sufficiently long period of time. Diabase dike intrusion may have promoted an unusually strong convection-driven circulation of fluids in the serpentinite shear zone.

How can the strong dependence of the chemical composition of josephinite on temperature of formation be accounted for? Chamberlain (1965) reacted magnetite, pentlandite, chalcopyrite, and pyrrhotite with moist hydrogen at different temperatures to determine at what temperatures these minerals are reduced to native metals. Magnetite, pentlandite, and chalcopyrite were reduced at 350°C and pyrrhotite at 385°C using one particular gas ratio of H_2O/H_2 (fig. 3). The gas compositions and temperatures at which magnetite and native iron can coexist had been determined by other workers previously, and Chamberlain experimentally determined that the sulfide-native metal equilibrium would be virtually superimposed upon it (fig. 3, line ABC). The slightly higher reduction temperature of pyrrhotite (fig. 3, line DEF) creates a narrow field in which pyrrhotite coexists with native metals. To the right of this field (at higher

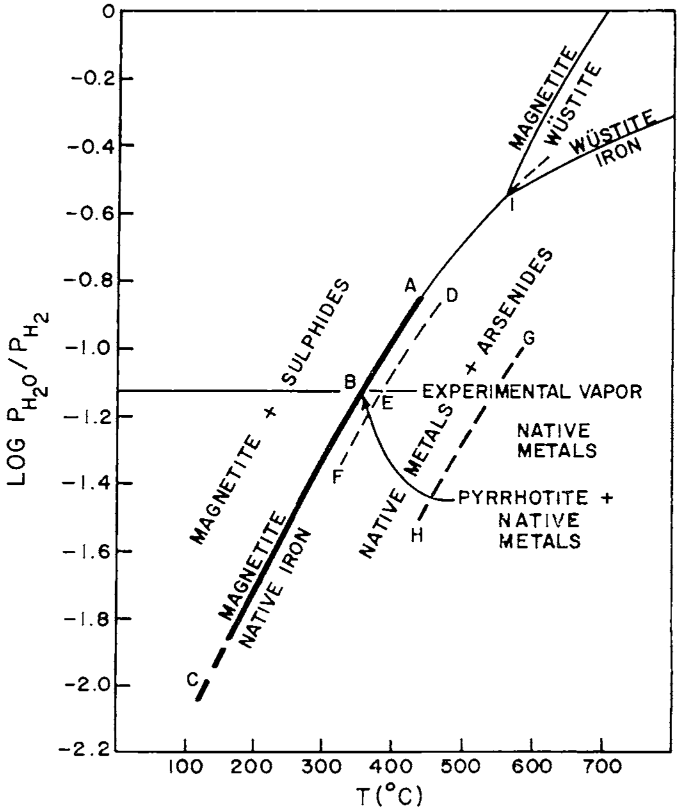


Fig. 3. Log pH_2O/pH_2 versus temperature diagram after Chamberlain and others (1965). The present authors have added line GH, creating a stability field of native metals and arsenides.

temperatures and lower pH_2O/pH_2 ratios) sulfide minerals and magnetite are unstable and should be consumed in forming native metals.

Sulfides and magnetite are very rare or absent in josephinite specimens formed above about 425°C (fig. 2). If, at this temperature, sulfides, magnetite, and native metals began to form together in equilibrium as suggested by the present study, a gas composition of pH_2O/pH_2 of about 1:8 was required. At higher temperatures, the gas composition may have been at an even lower ratio of pH_2O/pH_2.

Although the authors know of no experimental reduction study performed on nickel arsenide minerals, secondary nickel arsenides are dominant in josephinites formed above 400°C. The equilibrium curve for the coexistence of native metal and arsenides, then, should parallel that of sulfides and magnetite but be displaced some unknown distance toward higher temperatures and lower ratios of pH_2O/pH_2 (fig. 3, line GH). (Arsenides would be somewhat more difficult to reduce to metal than sulfides.) This displacement would result in the establishment of two very different chemical regimes under which metal may form during serpentinization. At higher temperatures ($\geqslant$ about 400°C) and at higher hydrogen activity, hydrothermal fluids involved in serpentinization will be precipitating native metals with secondary arsenides (providing a source of the metals and arsenic is available). At lower temperatures ($\leqq$ about 400°C) and at lower hydrogen activity, the fluids will precipitate native metals with magnetite and secondary sulfides. If temperature and/or hydrogen activities are low enough, native metals will not form at all, but a series of secondary sulfides will be deposited with magnetite.

The minor and trace element chemistry of the native metal products formed under the former regime are dominated by arsenic; the chemistry of the latter, by sulfur. In addition, calcium silicates (andradite, diopside) are the principal silicate minerals associated with the metal formed in the arsenic regime, and magnesium silicate (serpentine) is found mainly in products of the sulfur regime. Josephinites formed under the arsenic-calcium chemical regime are surprisingly rich in Pd and contain appreciable Te and Sb (table 4). The abundance of Bi in josephinite seems to "peak" in specimens formed just above about 450°C. These elements are apparently mobilized and redeposited during the initial stages of serpentinization (at high temperature). Pd, Te, and Sb are concentrated an order of magnitude or more above their abundance in the specimens formed under the sulfur-magnesium regime. Specimens formed under this regime display much higher abundances of the chalcophile elements, particularly Cu, Ag, Zn, and Pb.

Josephine County is apparently the only occurrence of native nickel-iron where specimens have been found that formed in the higher temperature, more strongly reducing arsenic-calcium metallogenic regime. The authors believe this adequately accounts for nearly all the observed characteristics of josephinite and its differences with respect to all other occurrences of terrestrial native nickel-iron.

CONCLUSIONS

Josephinite is uniquely different from all other reported occurrences of terrestrial native nickel-iron:

Many specimens consist of Ni-rich taenite and awaruite displaying crystallographically oriented intergrowths with andradite garnet. Andradite has not been reported associated with native nickel-iron (awaruite) from any other locality. The authors know of no previous discovery of terrestrial taenite. Specimens showing the taenite, awaruite, andradite intergrowths probably formed above about 450°C. The original metal was a single phase, taenite.

Josephinite formed over a range of temperatures (from nearly 500°C to below 350°C) in a chemically evolving serpentinization environment. Specimens formed near the top of this range display mineral assemblages, textures, and a chemical composition dramatically different from other occurrences of native nickel-iron. Specimens formed at the low temperature end of this range contain only awaruite, displaying associated minerals and textures more typical of the worldwide occurrences of this mineral. The chemical composition of these specimens parallels that of New Zealand awaruite.

Higher temperatures and more strongly reducing conditions resulted in the establishment of a metallogenic environment dominated by arsenic, under which nickel-iron containing trace elements carried along by arsenic, deposited with secondary arsenide minerals. At lower temperatures, the formation and chemistry of josephinite was dominated by the influence of sulfur similar to the many other well documented occurrences of native metals formed during serpentinization.

The authors recommend that the name "josephinite" be retained for the native-metal-rich metamorphic-metasomatic rocks described above. "Awaruite from Josephine County" cannot easily be used to describe native nickel-iron and andradite in specimens where awaruite may not be the original or even the most abundant metal present. It is conceivable that other localities for josephinite will be discovered in the future.

ACKNOWLEDGMENTS

We are indebted to K. F. J. Heinrich of the National Bureau of Standards and H. Winchell of Yale University for the electron microprobe measurements. Many thanks are owed to R. A. Nadkarni, J. F. Jaworski, G. J. Scilla, N. G. Howell, and J. D. Ganjei of Cornell University for their contributions to the chemical analysis of josephinite. M. E. Rich and B. F. Mentzen of Cornell University kindly assisted in the collection and interpretation of X-ray data. J. M. Bird of Cornell University supplied several samples for study. B. Bonnichsen, Cornell University, as well as H. J. B. Dick, H. Winchell, and D. M. Burt of Yale University contributed their expertise in helpful discussions and suggestions concerning this paper.

This work was supported in part by the National Science Foundation under Grant No. GP-30940X and through the Cornell Materials Science Center.

REFERENCES

Albee, A. L., and Chodos, A. A., 1970, Semiquantitative electron microprobe determination of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} in oxides and silicates and its application to petrologic problems: Am. Mineralogist, v. 55, p. 491-501.

Barnes, I., Rapp, J. B., and O'Neil, J. R., 1972, Metamorphic assemblages and the direction of flow of metamorphic fluids in four instances of serpentinization: Contr. Mineralogy Petrology, v. 35, p. 263-276.

Bowen, N. L., and Tuttle, O. F., 1949, The System $MgO–SiO_2–H_2O$: Geol. Soc. America Bull., v. 60, p. 439-460.

Buseck, P. R., Holdsworth, E., and Scott, R. G., 1973, The question of Eaton: terrestrial versus meteoritic copper: Geochim. et Cosmochim. Acta, v. 37, p. 1249-1254.

Challis, G. A., and Long, J. V. P., 1964, Wairauite—a new cobalt–iron mineral: Mineralog. Mag., v. 33, p. 942-948.

Chamberlain, J. A., 1966, Heazlewoodite and awaruite in serpentinites of the Eastern Townships, Quebec: Canadian Mineralogist, v. 8, p. 519-522.

——— 1967, Sulfides in the Muskox intrusion: Canadian Jour. Earth Sci., v. 4, p. 105-153.

Chamberlain, J. A., McLeod, C. R., Traill, R. J., and LaChance, G. R., 1965, Native metals in the Muskox intrusion: Canadian Jour. Earth Sci., v. 2, p. 188-215.

Coleman, R. G., 1967, Low-temperature reaction zones and Alpine ultramafic rocks of California, Oregon and Washington: U.S. Geol. Survey Bull. 1247, 49 p.

Dick, H. J. B., 1973, K–Ar dating of intrusive rocks in the josephine peridotite and rogue formation west of Cave Junction, southwestern Oregon: Geol. Soc. America Abs., v. 5, p. 33.

——— 1974, Terrestrial nickel iron from the josephine peridotite, its geologic occurrence, associations, and origin: Earth Planetary Sci. Letters, v. 24, p. 291-298.

Eckstrand, O. R., 1975, The Dumont serpentinite: a model for control of nickeliferous opaque mineral assemblages by alteration reactions in ultramafic rocks: Econ. Geology, v. 70, p. 183-201.

Geller, S., 1967, Crystal chemistry of the garnets: Zeitschr. Kristallographie, v. 125, p. 1-47.

Goldstein, J. I., 1973, Fe–Ni (Iron–Nickel), *in* Metals Handbook, v. 8, 8th ed.: Metals Park, Ohio, Am. Soc. Metals, p. 304-324.

Hultin, I., 1968, Awaruite (josephinite), a new mineral for Norway: Norsk. geol. tidsskr., v. 48, p. 179-185.

Jaffe, H. W., 1951, The role of yttrium and other minor elements in the garnet group: Am. Mineralogist, v. 36, p. 133-155.

Jamieson, G. S., 1905, On the natural iron–nickel alloy, awaruite: Am. Jour. Sci., 4th ser., v. 19, p. 413-415.

Kitahara, S., Takenouchi, S., and Kennedy, G. C., 1966, Phase relations in the system $MgO–SiO_2–H_2O$ at high temperatures and pressures: Am. Jour. Sci., v. 264, p. 223-233.

Krishnarao, J. S. R., 1964, Native nickel–iron alloy, its mode of occurrence, distribution and origin: Econ. Geology, v. 59, p. 443-448.

Melville, W. H., 1892, Josephinite, a new nickel iron: Am. Jour. Sci., 3d ser., v. 43, p. 509-515.

Moore, C. B., 1971, Nickel, *in* Mason, B., ed., Handbook of Elemental Abundances in Meteorites: New York, Gordon and Breach Sci. Publishers, p. 221-228.

Nickel, E. H., 1959, The occurrence of native nickel–iron in the serpentine rock of the eastern townships of Quebec Province: Canadian Mineralogist, v. 6, p. 307-319.

Palache, C., Berman, H., and Frondel, C., 1944, Dana's System of Mineralogy, v. 1, 7th ed.: London, John Wiley & Sons, Inc., p. 117.

Parthe, E. and Crocket, J. H., 1972, Platinum, in Wedepohl, K., ed., Handbook of Geochemistry: Berlin, Heidelberg, Springer-Verlag, p. F11.

Ramdohr, P., 1950, Über Josephinit, Awaruit, Souesit, ihre Eigenschaften, Entstehung und Paragenesis: Mineralog. Mag., v. 12, p. 374-394.

——— 1967, A widespread mineral association connected with serpentinization with notes on some new or insufficiently defined minerals: Neues. Jahrb. Mineralogie Abh., v. 107, p. 241-265.

Scarfe, C. M., and Wyllie, P. S., 1967, Serpentine dehydration curves and their bearing on serpentinite deformation in orogenesis: Nature, v. 215, p. 945-946.

Thayer, T. P., 1966, Serpentinization considered as a constant-volume metasomatic process: Am. Mineralogist, v. 51, p. 685-710.

Torok, T. E., 1973, Co-Fe (Cobalt-Iron), *in* Metals Handbook, v. 8, 8th ed.: Metals Park, Ohio, Am. Soc. Metals, p. 287, 354.

Ulrich, G. H. F., 1891, On the discovery, mode of occurrence, and distribution of the nickel-iron alloy awaruite, on the west coast of the South Island of New Zealand: Geol. Soc. London Quart. Jour., v. 46, p. 619-633.

Viting, L. M., 1957, Study of the iron-nickel-cobalt system in the region of the intermetallic compounds Ni_3Fe and FeCo. I. The intermetallic compound Ni_3Fe and its region of existence in the iron-nickel system: Zhur. Neorg. Khim., v. 2, p. 367-374.