



CANADA

THE OCCURRENCE OF NATIVE NICKEL-IRON
IN THE SERPENTINE ROCK OF THE
EASTERN TOWNSHIPS OF QUEBEC PROVINCE

by

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THE OCCURRENCE OF NATIVE NICKEL-IRON IN THE SERPENTINE ROCK OF THE EASTERN TOWNSHIPS OF QUEBEC PROVINCE¹

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ABSTRACT

Native nickel-iron has been found over a wide area in the serpentized asbestos-bearing rock of the Eastern Townships of Quebec. The chemical composition (average of two analyses) is: nickel 71.0%, iron 25.3%, cobalt 3.5%, and copper 0.2%. The nickel-iron forms a single-phase alloy with a face-centred cubic structure and a cell constant which varies from 3.551 to 3.555 Å. It occurs chiefly as tiny spheroidal grains, most of which are less than 10 microns in diameter, but also as larger crenulated grains up to 100 microns in diameter, and as acicular crystals up to 100 microns in length. The nickel-iron appears to have been formed as the result of the breakdown, during serpentinization of primary olivine and enstatite containing about 0.2% combined nickel.

INTRODUCTION

Terrestrial nickel-iron has been found in a number of localities, but almost all the occurrences are in unconsolidated sediments. It has been found as grains and scales in alluvial deposits, as, for example, in the Gorge river at Awarua Bay, New Zealand, in the Fraser river of British Columbia, or in the Brokovka river in the Urals of the U.S.S.R., and it may occur in large boulders, as, for example, in Josephine and Jackson counties, Oregon. There are only rare reports of nickel-iron *in situ* (Ramdohr, 1950). The composition of terrestrial nickel-iron found to date ranges from 65 to 75% nickel and 25 to 35% iron. The mineral names given to this material reflect the geographical locale of the occurrences, and include awaruite, josephinite, souesite and brokovkite, although, on the basis of chemical composition, they all probably represent the same species. Awaruite was the first name applied to native nickel-iron of this composition, and therefore it deserves priority.

It has been known for some years that the host rocks of the asbestos deposits in the Eastern Townships of Quebec contain an appreciable amount of nickel. The distribution of this element is very uniform, for analyses of asbestos tailings over several decades show that the nickel

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content ranges between 0.2 and 0.3 per cent. As a result of mineralogical investigations, the nickel was found to occur, at least in part, as native nickel-iron. To the best of our knowledge it was first separated and identified in 1938 in asbestos tailings of the Canadian Johns-Manville Company, by Dr. M. H. Haycock, Head of the Ore Mineralogy Section of the Mineral Dressing and Process Metallurgy Division of the Mines Branch at Ottawa (Mines Branch Mineragraphic Report M-597-R).

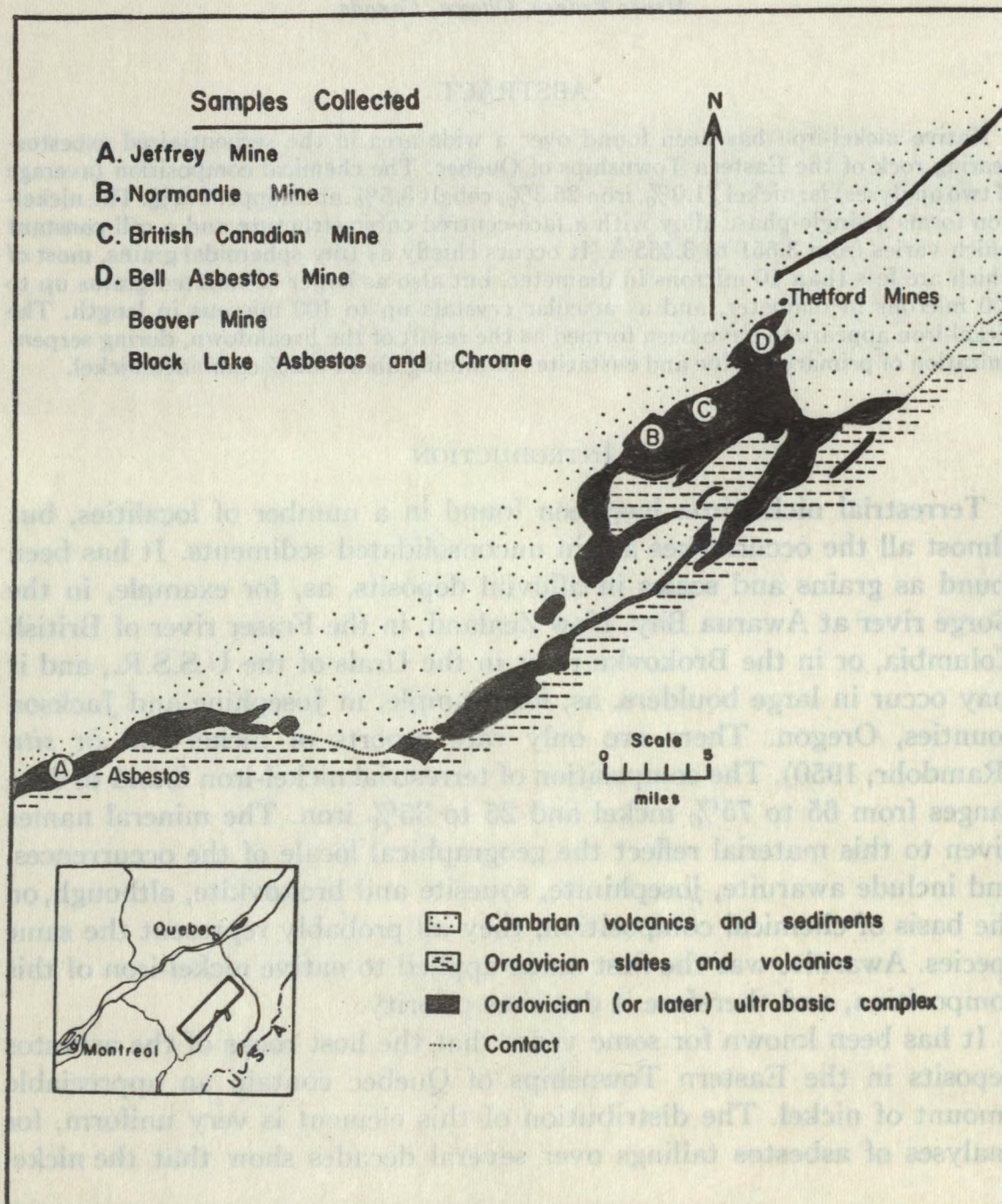


FIG. 1. Sketch map of the "asbestos belt" of the Eastern Townships of Quebec, showing the distribution of the ultrabasic bodies and the location of the samples collected. (After Riordon, 1957.)

In a field trip to the area in 1957, rock samples were collected by the author from a number of the properties and operating mines, in order to determine whether the occurrence of the nickel-iron is general throughout the "asbestos belt". Specimens, selected with a view to obtaining examples of all degrees of serpentinization, were collected from the Jeffrey Mine of the Canadian Johns-Manville Company Limited at Asbestos, Quebec, and from the following properties in the Thetford Mines area: Bell Asbestos Mines Limited; the Black Lake Asbestos and Chrome property; and the Beaver, Normandie, and British-Canadian Mines of Asbestos Corporation Limited. These properties span a distance of about 40 miles, and are shown in the sketch map (Fig. 1).

OCCURRENCE

The widespread occurrence of the native nickel-iron is attested to by its presence in every one of twenty-four polished sections prepared from the samples.

The rocks in which the nickel-iron occurs are dunites and peridotites, all of which are extensively serpentinized. The principal minerals present are the serpentine minerals chrysotile and antigorite, and most of the samples collected also contain irregularly distributed brucite, magnetite and chromite. A few of the samples contain remnants of partially serpentinized enstatite and olivine, as well.

The nickel-iron is found almost exclusively in the chrysotile and antigorite, only rarely in the magnetite, and not at all in enstatite, olivine, or chromite. It occurs principally as tiny spheroidal or crenulated grains less than 10 microns in diameter (Fig. 2), and where it is abundant in transparent serpentine it has the appearance of fine metallic dust. Larger grains are also present, and these are always deeply crenulated (Figs. 3 and 4). The largest grain observed was 0.1 mm in diameter. In a few specimens the nickel-iron also occurs as tiny needles up to 100 microns long and 10 microns wide (Fig. 2).

CHEMICAL AND PHYSICAL PROPERTIES

The samples of nickel-iron analyzed (Table 1) were concentrated by means of wet tabling, magnetic concentration and superpanning of asbestos tailings obtained from the Canadian Johns-Manville mill at Asbestos, Quebec. The first sample of native nickel-iron (analysis I) was concentrated in 1938 by Dr. M. H. Haycock, and the second one (analysis II) was prepared in 1958 under direction of the author. All the physical properties discussed below were determined from sample II.



FIG. 2. Photomicrograph of polished section of serpentized rock from the Bell Asbestos Mines Limited, showing the occurrence of numerous tiny grains of nickel-iron alloy. One of the grains has an acicular shape. Magnified 185 \times .



FIG. 3. Photomicrograph of polished section of serpentized rock from the Jeffrey Mine of the Canadian Johns-Manville Company Limited, showing a large grain of nickel-iron. Note the highly crenulated outline of the grain. Magnified 370 \times .



FIG. 4. Photomicrograph of polished section of serpentinized rock from the Jeffrey Mine, showing a large irregular grain of nickel-iron. Magnified 465X.

TABLE 1. CHEMICAL ANALYSIS OF NATIVE NICKEL-IRON FROM THE CANADIAN JOHNS-MANVILLE COMPANY LIMITED

	Chemical Analyses		Recalculated after Subtraction of the Insoluble Residue	
	I	II	I	II
Fe	25.19%	23.63%	25.26%	25.40%
Ni	70.18	66.55	70.38	71.53
Co	4.04	2.68	4.05	2.88
Cu	0.31	0.18	0.31	0.19
Insol.	0.66	7.17		
TOTAL	100.38	100.21	100.00	100.00

In the analysis of sample II the solvent used was anhydrous methanol and iodine, since tests on synthetic mixtures had shown that this solvent dissolves the metallic components while leaving the silicates unattacked. An *x*-ray diffraction pattern of the undissolved residue of sample II matches that of chrysotile, and a chemical analysis of the residue shows that magnesia and silica are present in about the correct ratio for chrysotile. The presence of this chrysotile can be attributed to inclusions in the nickel-iron. This is to be expected, since only grains larger than 325 mesh (45 microns) were concentrated, and these are severely crenu-

lated, as noted above. Sample I has a relatively small amount of insoluble residue, because this concentrate was ground in an agate mortar to free as much of the adhering serpentine as possible before analysis.

The analysis of the insoluble residue of sample II also showed the presence of 0.87% Ni and 0.34% Fe. Since this Ni:Fe ratio is similar to that in the soluble portion, it is assumed that these elements in the insoluble residue are due to metallic inclusions within the chrysotile particles. If this assumption is correct, the amount of chrysotile in sample II equals the percentage of the insoluble residue minus the nickel and iron in the residue, or $7.17 - 1.21 = 5.96\%$. The exact amount of chrysotile present in the analyzed sample is important in determining the specific gravity of the nickel-iron, as will be shown later.

The nickel-iron in the samples studied is a single-phase alloy with a face-centred cubic structure. The cell constant of the material analyzed is 3.555 Å, while those of other samples of nickel-iron collected range downward to 3.551 Å. The cell constant of 3.555 Å corresponds to that of a nickel-iron alloy containing 74 atomic per cent nickel and 26 atomic per cent iron (from Bradley *et al.* 1937, assuming their measurements to be in kX units). This corresponds very closely to the atomic percentages obtained from the analysis of sample II, which are shown in Table 2, if the cobalt and copper are grouped with the nickel.

The x-ray powder pattern of the alloy, if overexposed to cobalt radiation, exhibits weak superlattice lines which correspond to the superlattice in slow-cooled artificial Ni_3Fe , first reported by Leech & Sykes (1939). The presence of these lines indicates that the metal atoms occupy ordered positions in the lattice. A face-centred unit cell contains 4 atoms, one being located at the cube corner and the other three at the cube faces. The consistent Ni:Fe ratio of about 3:1 of this nickel-iron alloy and of others reported in the literature suggests that the iron atoms form a primitive cubic lattice, while the nickel atoms occupy the face-centred positions. This ordered arrangement may explain the relatively uniform composition of terrestrial nickel-iron.

The calculations involved in determining the atomic percentages of the elements in the alloy and its molecular weight from analysis II are shown in Table 2. In column 5 the atomic proportions have been calculated to total 4.00 because the nickel-iron, being face-centred, contains 4 metal atoms per unit cell. The molecular weight is the sum of the weights of the atoms shown in the final column, or 231.9.

The specific gravity of sample II, as determined by pycnometer, is 7.44. After correcting for the 5.96% chrysotile with an assumed specific gravity of 2.40, the specific gravity of the alloy alone is 8.58. The theoretical specific gravity calculated from the molecular weight M , and

the volume of the unit cell V , is $\rho = \frac{M \times 1.6602}{V} = \frac{231.9 \times 1.6602}{(3.555)^3} =$

8.57, which agrees very closely with the determined specific gravity.

The hardness of the nickel-iron, as determined by diamond indentation using a Wilson-Tukon hardness tester, is DHN 209, which corresponds to about 4.5 on Mohs' hardness scale.

TABLE 2. CALCULATION OF THE ATOMIC PERCENTAGES AND MOLECULAR WEIGHT OF THE NICKEL-IRON

Metal	Wt. % (Anal. II)	Atomic proportions	Atomic %	No. of atoms in unit cell	Wt. of atoms in unit cell
Fe	25.40	0.455	26.4	1.06	59.2
Ni	71.53	1.218	70.6	2.82	165.6
Co	2.88	0.049	2.8	0.11	6.5
Cu	0.19	0.003	0.2	0.01	0.6
TOTAL	100.0	1.725	100.0	4.00	231.9

ORIGIN OF THE NICKEL-IRON

As mentioned above, microscopic examination of the polished sections shows that the nickel-iron does not occur in the primary silicates olivine and enstatite but is restricted almost exclusively to the serpentine minerals. This can be seen in Figs. 5 and 6, which show the primary silicates in different stages of serpentinization. This admits of only two possibilities: either the nickel was introduced during serpentinization, or it was present in some form in the primary rock and was later transformed into nickel alloy during serpentinization. In an attempt to determine which is more probable, samples of the olivine and enstatite, assumed to be the primary rock silicates, were analyzed for nickel. The procedure was as follows: olivine and enstatite were concentrated from incompletely serpentinized rock by crushing the rock to $-150+200$ mesh and separating the components by heavy liquids. The olivine and enstatite concentrates were then ground in a mechanical mortar for one hour, and analyzed for total and metallic nickel. The metallic nickel contents were determined by the anhydrous methanol and iodine method noted previously.

The analyses (Table 3) show that the olivine and pyroxene concentrates, with one exception, contain in the neighbourhood of 0.2% nickel, which is approximately that of the rock as a whole. The metallic nickel content is very low and can be attributed, at least in part, to native metal in microscopic serpentine veinlets which have not been entirely separated from the primary silicates.



FIG. 5. Photomicrograph of a polished section of a rock from the Jeffrey Mine, showing veinlets of serpentine in enstatite. Grains of nickel-iron (white) can be seen in the serpentine veinlets, but are absent in the enstatite. Magnified 185 X.

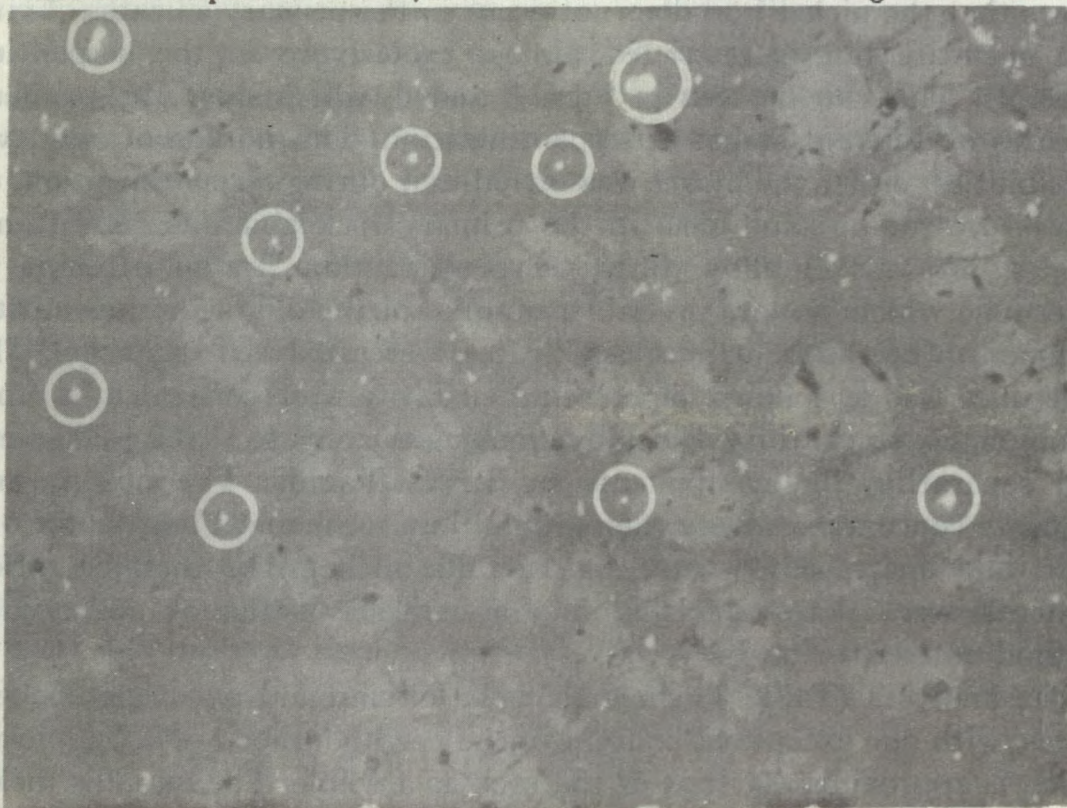


FIG. 6. Photomicrograph of a polished section of partially serpentinized rock from the Bell Asbestos Mines Limited, showing remnants of olivine (medium grey) in a serpentine matrix (dark grey). Magnetite (light grey) and nickel-iron (white, circled) occur only in the serpentine, and exhibit a close similarity in grain size and distribution, indicating a common origin. Magnified 185 X.

TABLE 3. THE NICKEL CONTENT OF OLIVINE AND ENSTATITE CONCENTRATES

Sample No.	Description of sample	Nickel content	
		(Total %)	(Metallic %)
JM-8	Enstatite from the Jeffrey Mine	0.064	0.012
AC-9	Olivine from the Black Lake Asbestos and Chrome property	0.24	0.020
AC-10	Olivine with enstatite, from the British-Canadian Mine	0.26	0.024
AC-12	Enstatite with olivine, from the Normandie Mine	0.18	0.020

Since microscopic examination of polished sections of the olivine and enstatite did not reveal the presence of separate nickel minerals, we must conclude that the nickel is present in the mineral structures, probably in substitution for magnesium. From the fact that the nickel content of the olivine and enstatite is approximately equal to that of the serpentinized rock as a whole, we can further conclude that all, or practically all, of the nickel in the rock was originally present in the primary silicates.

Serpentine from the same samples was also analyzed for metallic and total nickel. In this case, only relatively large grains (greater than 0.1 mm) were concentrated, to ensure that the particles of nickel-iron present in the serpentine would be concentrated with it. After concentration, the serpentine samples were ground for one hour, in order to give the solvent complete access to the metal inclusions. The results, listed in Table 4, show that the nickel content of the alloy-containing serpentine is also in the neighbourhood of 0.2%, which indicates that no appreciable nickel has been gained or lost during serpentinization of the primary silicates.

TABLE 4. THE NICKEL CONTENT OF THE ALLOY-CONTAINING SERPENTINE CONCENTRATED FROM THE SAMPLES LISTED IN TABLE 3

Sample No.	Total Ni (%)	Metallic Ni (%)
JM-8	0.15	0.10
AC-9	0.19	0.10
AC-10	0.21	0.10
AC-12	0.21	0.03

The amount of metallic nickel in the serpentine indicates that, in the majority of the samples, about one-half of the nickel is present as metal and the remainder is presumably contained in the serpentine mineral structures. One sample (AC-12) contains considerably less metallic nickel than the others, although its total nickel content is similar to that of the other samples. This shows that the amount of nickel held in the serpentine structure may be variable.

It may be concluded, therefore, that olivine and enstatite accept essentially all the nickel (0.2%) into their structures, whereas the serpentine minerals accept only about half this amount. The behaviour of nickel is somewhat similar to that of iron, since the latter element is also largely rejected by the serpentine minerals during serpentinization, resulting in the formation of magnetite, characteristically present in serpentinized rock. The geochemical similarity of nickel and iron can be attributed to their similar electronegativities—1.7 and 1.65 for divalent nickel and iron respectively (Ringwood, 1955). Magnesium, however, has a much lower electronegativity—1.2, with the result that it forms hydrous silicates (the serpentine minerals) which exclude the majority of the nickel and iron.

On the other hand, garnierite, which is composed of one or more nickel-bearing serpentine minerals, is believed to contain the nickel in its structure. In fact, Noll & Kircher (1952) have synthesized the pure nickel end-member of garnierite, in which all the magnesium has been replaced by nickel, and they report that its *x*-ray pattern is identical to that of chrysotile. They conclude from this that nickel can replace magnesium in all proportions in chrysotile. That it has not done so in the serpentinized rocks in the eastern townships of Quebec must be due to the particular conditions of composition, temperature, pressure, and/or time, prevailing during serpentinization.

Although only a few occurrences of native nickel-iron have been reported, thermodynamic calculations show that nickel-iron can exist in equilibrium with magnetite. In Fig 7 the activity of iron is shown plotted against temperature for Ni_3Fe (I) and $\text{Fe}_3\text{O}_4\text{-FeO}$ (II). According to this plot, Ni_3Fe is in equilibrium with magnetite below 750°C , while above this temperature it is in equilibrium with FeO. (The designation "FeO" is used to indicate the wüstite phase which is of variable composition FeO_x , where *x* depends on the temperature and oxygen partial pressure.)

Unfortunately, there are very few thermodynamic data available on systems involving the serpentine minerals. However, some light may be shed on the serpentinization process by an evaluation of the temperature-gas pressure relationships for Ni_3Fe in equilibrium with magnetite, since it appears that the nickel-iron and magnetite were formed during serpentinization. Jander & Wuhrer (1938), as a result of hydothermal experiments dealing with the formation of serpentine from olivine and enstatite, concluded that the formation of serpentine depends to a large extent on the amount of hydrogen and water available.

The $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio for the $\text{Ni}_3\text{Fe}\text{-Fe}_3\text{O}_4$ equilibrium can be calculated from data given by Darken & Gurry (1945) and by Kubaschewski & von Goldbeck (1949), and is plotted in Fig. 8, together with the curves

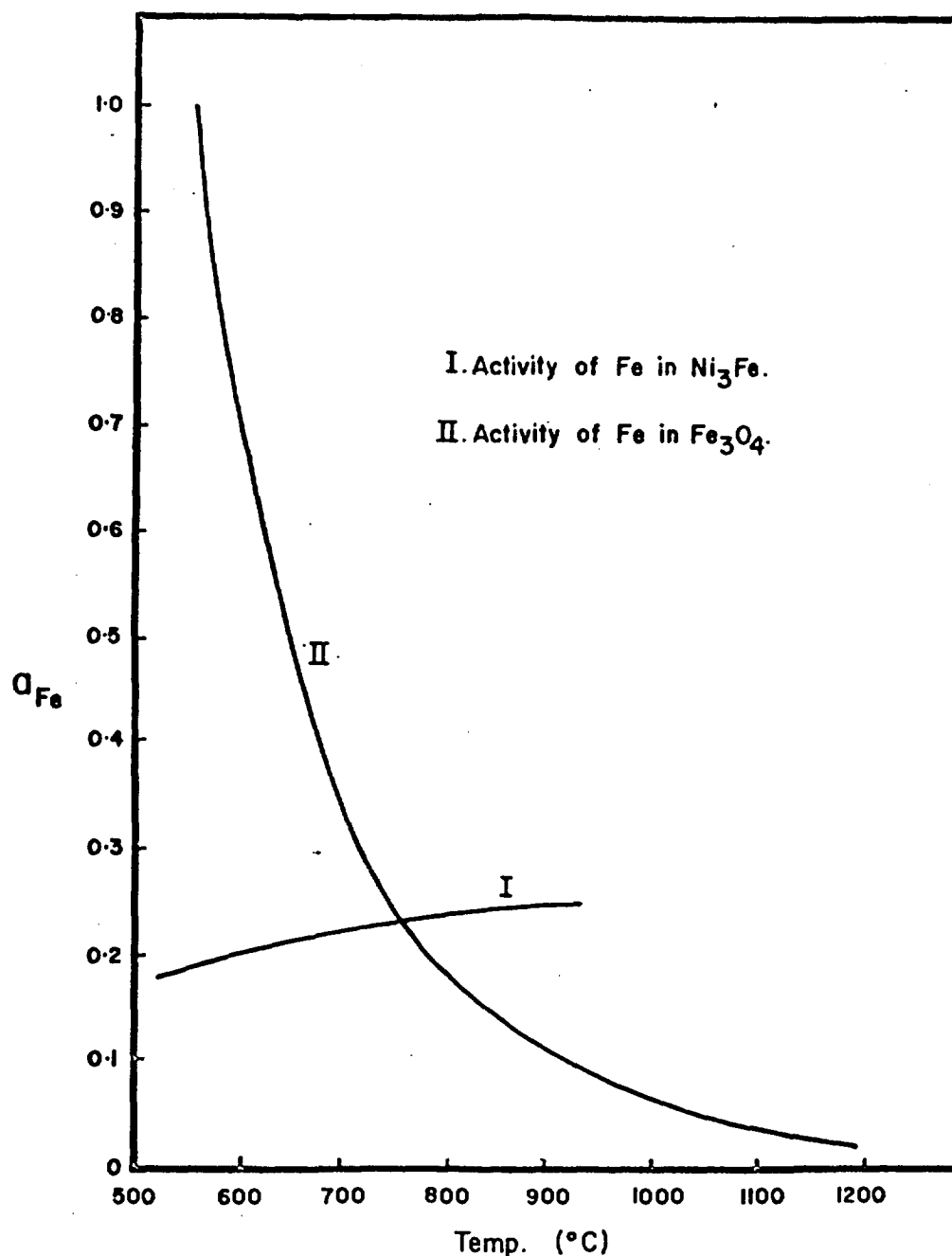


FIG. 7. The activity of iron in Ni_3Fe and in magnetite in equilibrium with wüstite; calculated from data given by Kubaschewski & von Goldbeck (1949) and Darken & Gurry (1945).

for $\text{Ni}_3\text{-Fe-FeO}$, $\text{FeO-Fe}_3\text{O}_4$, and FeO-Fe . (Data given by Oriani (1953) are not in complete agreement with those of Kubaschewski & von Goldbeck, particularly as regards the composition of Ni_2Fe at which magnetite becomes more stable than wüstite. However, the data of the latter appear to be more consistent with the data of Darken & Gurry, provided no nickel enters the magnetite.) It is evident from Fig. 8 that between 600°C and 750°C , $\log P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ for the $\text{Ni}_3\text{Fe-Fe}_3\text{O}_4$ equilibrium

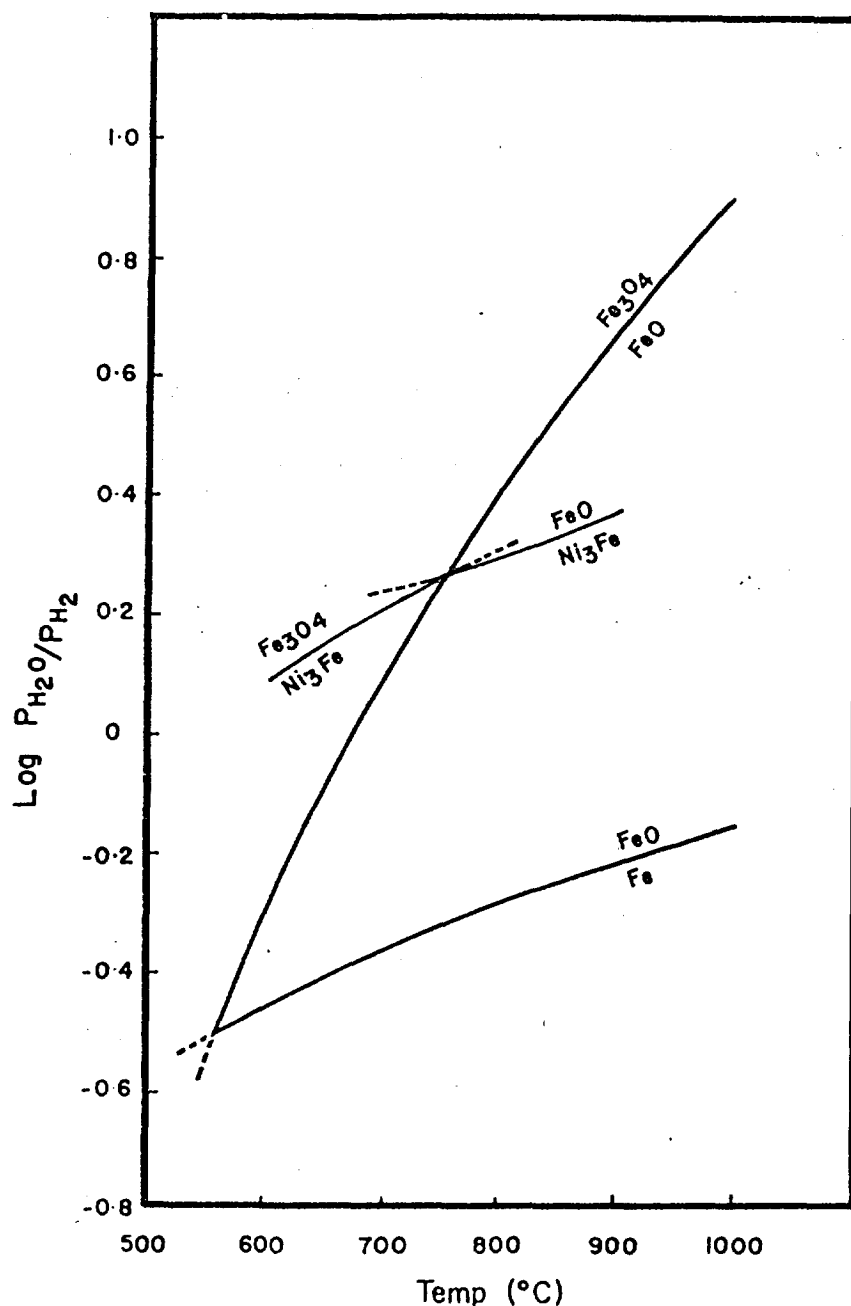


FIG. 8. The metal-oxide-gas equilibrium curves for $\text{Ni}_3\text{Fe}-\text{Fe}_3\text{O}_4$, $\text{Ni}_3\text{Fe}-\text{FeO}$, $\text{FeO}-\text{Fe}_3\text{O}_4$ and $\text{Fe}-\text{FeO}$, calculated from data by Darken & Gurry.

varies between 0.10 and 0.26, which is equal to the numerical $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratios of 1.3 and 1.8 respectively. Extrapolation of the curve to lower temperatures would result in a lower $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio. At temperatures above 750°C , magnetite is unstable in the presence of Ni_3Fe . The $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ values can be recalculated in terms of the partial oxygen pressure (P_{O_2}). The P_{O_2} values for Ni_3Fe and Fe_3O_4 in equilibrium are 2.1×10^{-24} at 600°C and 1.0×10^{-19} at 750°C .

A change in the composition of the nickel-iron can be expected to shift

the $\text{Ni}_3\text{Fe}-\text{Fe}_3\text{O}_4$ curve upward in the case of higher nickel content in the alloy, or downward in the case of lower nickel content. The slopes of these curves should closely parallel that of $\text{Ni}_3\text{Fe}-\text{Fe}_3\text{O}_4$ (or $\text{Ni}_3\text{Fe}-\text{FeO}$), as is the case with the $\text{Fe}-\text{FeO}$ curve shown in Fig. 8.

If the assumptions implicit in the application of thermodynamic calculations to the current problem are valid, then it is clear that the $\text{H}_2\text{O}/\text{H}_2$ ratio during the formation of the nickel-iron and magnetite had a maximum value of 1.8, the partial oxygen pressure P_{O_2} had a maximum value of 1.0×10^{-19} , and the maximum temperature of formation was 750°C . Since the nickel-iron and the magnetite appear to have formed during serpentinization, these values may give some clue to conditions existing during the formation of serpentine in the deposits from which the samples were taken, and may have some bearing on serpentinization processes generally.

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