

THE Ni, Fe AND Co CONTENTS OF METAL PHASES IN THE ALLENDE, HOLBROOK AND NUEVO MERCURIO CHONDRITES

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Abstract: The Ni, Fe and Co contents of metal phases in the Allende, Holbrook and Nuevo Mercurio chondrites have been obtained using an automated electron microprobe fitted with both wavelength and energy dispersive spectrometers.

The variation patterns of Ni-Fe-Co metal used in this study are discussed from the standpoints of the volume percentage and average composition of each region, and the overall average composition of the metal phases. An advantage of random selection of many analytical points is that bulk composition of plesite becomes apparent even when the scale of intergrowth is generally less than the beam diameter.

Co contents of kamacite in these chondrites are inconsistent with those reported previously, but the general tendency of Co to increase in the kamacite in chondrites from H, L to LL groups, is supported by this study.

Although the variation patterns of Ni-Co observed so far for L4, H5 and CV3 chondrites are simple, six L6 chondrites, including those reported previously, show significant difference in Co contents and the concentration and abundance characteristics of Ni-Fe-Co patterns of the metal phases.

The great similarity of composition of each region of these patterns obtained from two samples of Holbrook and two samples of Allende which came from different collections, indicates that the variation patterns of Ni-Co in the metal phases provide a means of characterization or "fingerprinting", as do the great differences in the variation patterns of Fe-Ni-Co which occur from one chondrite to another or even within the same group and petrologic type.

1. Introduction

The Ni-Fe metal phases in meteorites contain, in general, varying amounts of minor Co and traces of other elements. The proportions of these elements vary greatly not only from meteorite to meteorite but also from grain to grain and within grains. SMITH (1980) suggested that the pattern of variation, together with the average composition of the Ni, Fe and Co contents of these metal phases, may be useful in fingerprinting meteoritic materials, particularly chondrites, as well as offering information on the meteorite's formation processes (especially shock and/or thermal history). Such a technique could be also applied to establish affinities amongst large groups of mete-

orites such as those recovered from Antarctic blue ice. It may also be of use of solving problems concerning the identity of certain specimens collected from different localities or perhaps mislabelled specimens in meteorite collections.

In this study, the technique is used for investigating some well known chondrites prior to studying Antarctic meteorites which may have originated as fragments of single meteorites or from meteorite bodies with similar formation processes (*cf.* MIÚRA and MATSUMOTO, 1982). Such characterization requires careful determinations at several hundred analytical points on the various Fe-Ni-Co metal phases present, using an automated electron microprobe fitted with both an energy- and wavelength-dispersive spectrometers. This paper shows the tentative grouping of whole Ni-Fe-Co metallic regions and compares this data with data obtained previously by SMITH (1980) and SMITH and LAUNSPACH (1983).

2. Experimental

The samples used in this study are from three chondrites: Holbrook (L6), Nuevo Mercurio (H5) and Allende (CV3). The Allende-1 and Holbrook-1 samples are from the Yamaguchi University collections; and Allende-2 and Holbrook-2, from the University of Alberta collections. Data labelled "Allende-3" represents the compilation of data points for Allende-1 and -2.

The polished thin sections were analyzed at the University of Alberta using an Applied Research Laboratories (A. R. L.) "EMX" microprobe fitted with three wavelength-dispersive spectrometers and an Ortec energy-dispersive spectrometer. Subsequently, full automation of the procedure was achieved on a A. R. L. "SEM-Q" microprobe which has four wavelength-dispersive spectrometers and an Ortec "EEDS II" energy dispersive system. Throughout the work the instrument was operated at 15 kV accelerating voltage and 25 nA probe current as measured by a Faraday cage. The Ni and Co concentrations were determined by wavelength dispersive analysis (WDA) and Fe concentrations by energy dispersive analysis (EDA). Concentrations were measured against a series of standards including pure Ni, Fe and Co, and four intermediate Ni-Fe alloys. Because only two LiF crystal spectrometers were available, the third element of interest was determined by EDA. Fe was selected for EDA rather than Ni or Co because it is present in higher concentrations and because the Fe $K\alpha$ peak is free of the severe spectral interferences which affect the determination of Co & Ni in EDA. Furthermore, the use of EDA in this way not only permits the simultaneous determination of all three elements but also allows a rapid visual check of the X-ray spectra so that data from incorrectly identified grains can be rejected at the time of acquisition.

Fe, Ni and Co intensities are measured on as many randomly chosen sample points as possible in the metal phases. Instead of the normal procedures for fully quantitative analysis which involve the collection of full ZAF corrections, the "calibration curve" approach can be used without significant loss of accuracy provided that a series of standard materials covering the Fe-Ni composition range is available (SMITH and LAUNSPACH, 1983). A third order polynomial fit to standard Fe-Ni data is generated by the FORTRAN IV program "FENICO". The sample Co concentrations are de-

terminated by reference to a metal standard with empirical corrections for background and matrix effect made by the program. The program then produces output automatically as "raw" and 100%-normalized data. A few grains giving total weight percentages $(\text{Ni} + \text{Fe} + \text{Co}) < 95 \text{ wt } \%$ were ascribed to other phases or close to inaccurate analyses, and were rejected automatically from further data processing.

The selection of analytical points within grains is made randomly as far as possible, although there is undoubtedly a tendency to avoid the extreme margins. Inevitably some operator bias will enter into the choice. These tendencies may result in a slight distortion of the concentration characteristics and the average composition of overall metal phases, but in no serious distortion of the average compositions of each metal region.

3. Discussion

Typical grains of the metal phases in Holbrook and Allende are shown in the scanning images of Figs. 1 and 2. The Ni-Co variation diagrams obtained from Holbrook, Nuevo Mercurio and Allende, are shown in Figs. 3 to 8. Five different types of metal regions can be observed and have been designated kamacite, plessite, taenite, and Ni-rich phases I and II for the purposes of this study.

Figure 1 shows that within a single grain of Holbrook metal, regions of higher Ni and lower Co (taenite etc.), lower Ni and higher Co (kamacite) and plessite are observed. White regions in the backscattered electron image (BSE) are taenite; gray regions are kamacite; and domain-like regions of white and gray intergrowths (with individual component phases about $1 \mu\text{m}$ in width), are plessite. Two different metal regions can be observed in Fig. 2. The Ni-rich phases I and II are the gray and white regions, respectively, in the BSE.

3.1. Treatment of exsolution regions

Although there are four distinct Ni-Fe-Co metal phases (*i.e.*, kamacite, taenite, tetrataenite and awaruite), exsolution intergrowths are found in the region of plessite ($10 < \text{Ni} < 24$). Even if the electron microprobe is operated with a fully focussed ($< 1 \mu\text{m}$) beam, inadequate resolution of intergrowths can be expected. However, an advantage of the random analysis used in this study is that the bulk composition of plessite regions (or other intergrowths) become apparent even when the scale of the intergrowths is less than the beam diameter. Furthermore, it is apparent that the plessite seen in Holbrook (Figs. 3 and 4) is rare or absent in Nuevo Mercurio (Fig. 5).

The variation patterns of the Ni-Fe-Co metal phases investigated in this study are discussed from the following viewpoints:

- 1) volume percentages and average composition of each compositional region.
- 2) The overall average composition of the metal phase.

3.2. Variation patterns

Table 1 shows the volume percentages of five Ni-Fe-Co metal regions obtained for the Holbrook, Nuevo Mercurio and Allende chondrites. The corresponding average compositions of various Ni-Fe-Co metal phases are listed in Tables 2 and 3.

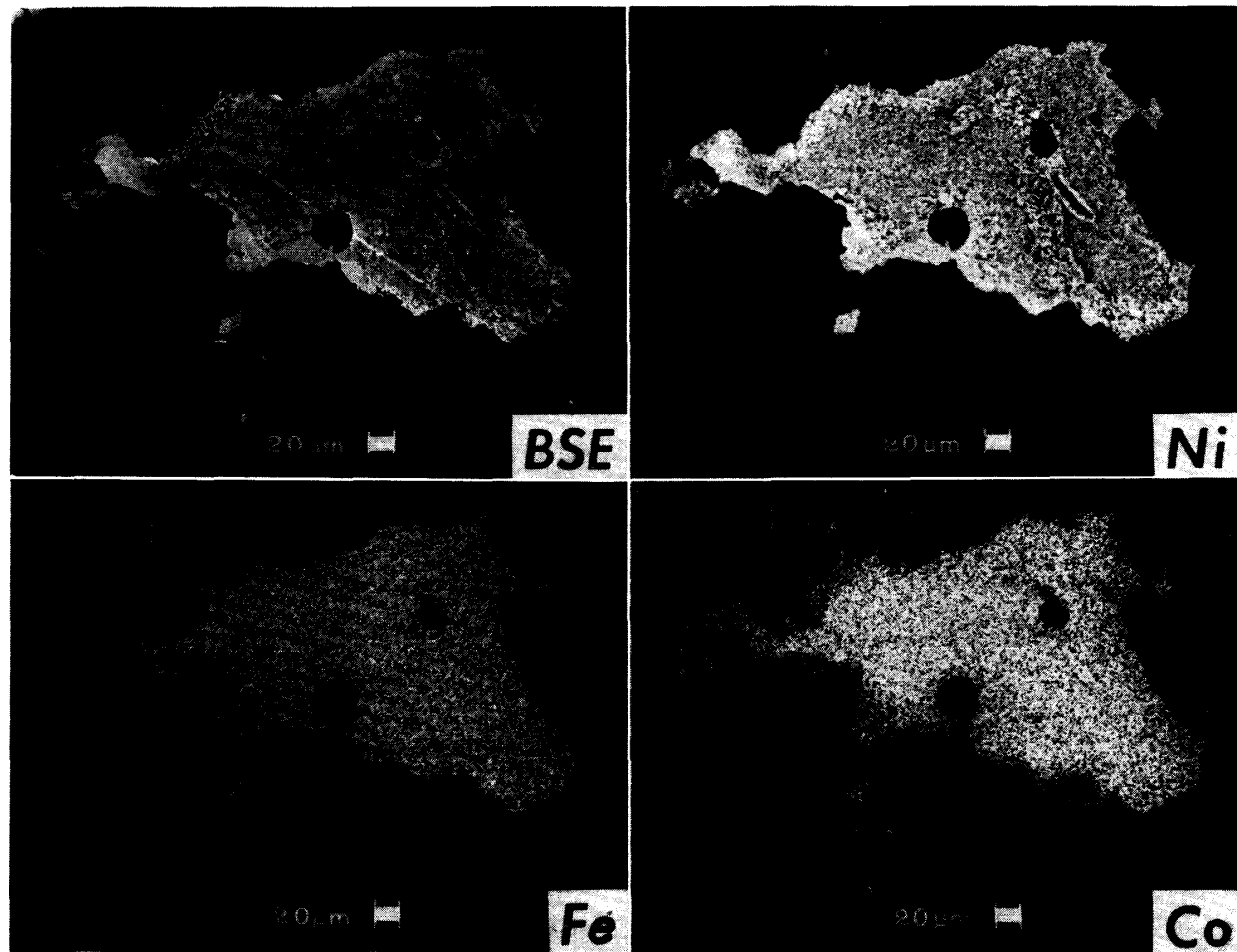


Fig. 1. Backscattered electron (BSE), Ni, Fe and Co images of a metal grain in Holbrook-I. Operating voltage is 15 kV. Note the extreme inhomogeneity which exists within a single grain. Magnification is indicated by scale bar of 20 μm . In the BSE image, the white region is a Ni-rich phase; gray, kamacite; white and gray domain-like lamellar region, plessite.

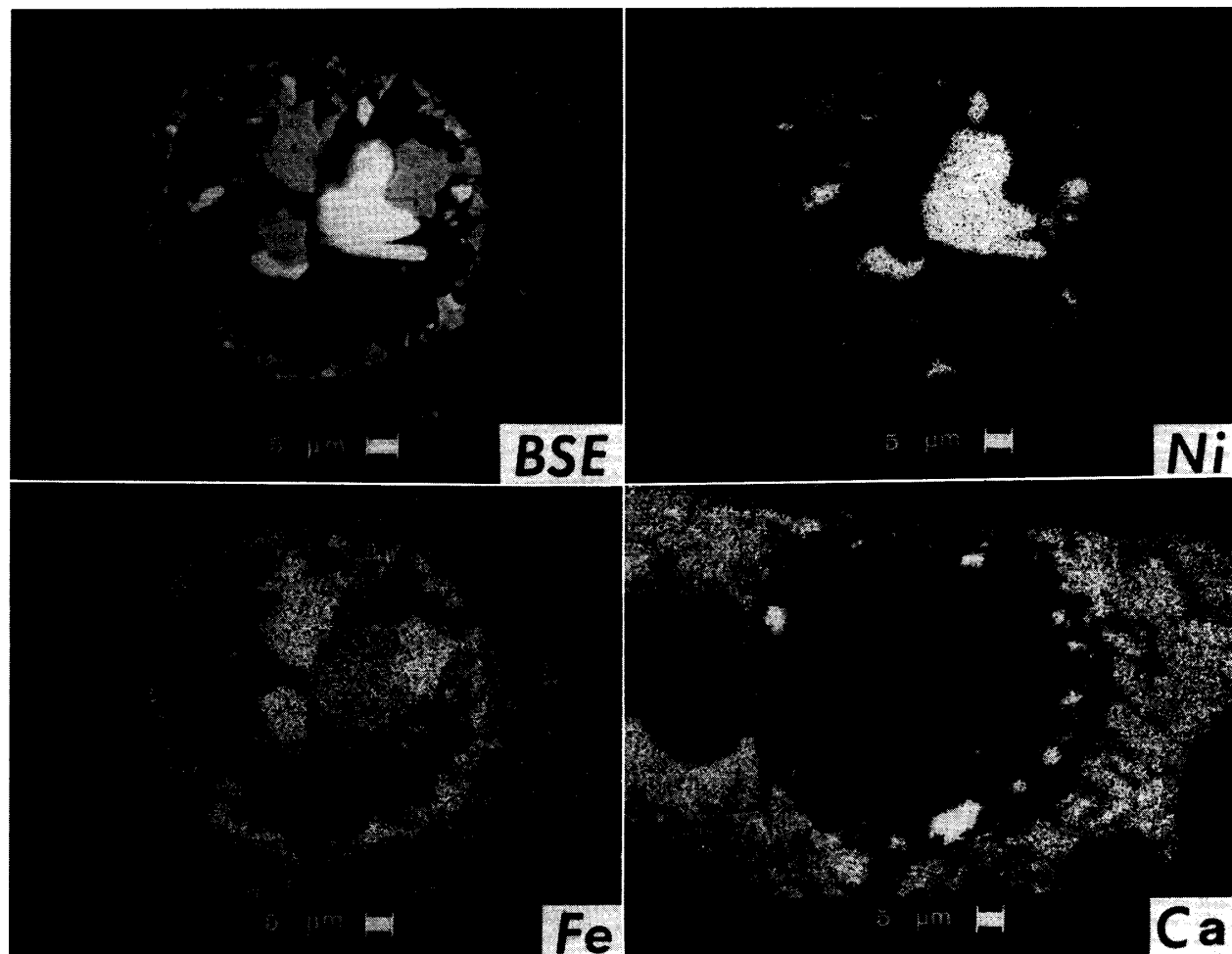


Fig. 2. Backscattered electron (BSE), Ni, Fe and Ca images of a chondrule in Allende-1. Operating voltage is 15 kV. Note the Ni-rich metal areas are homogeneous. Fe-rich areas are metal and sulphides. The very high Ca areas are phosphate grains. Magnification is indicated by scale bar of 5 μm .

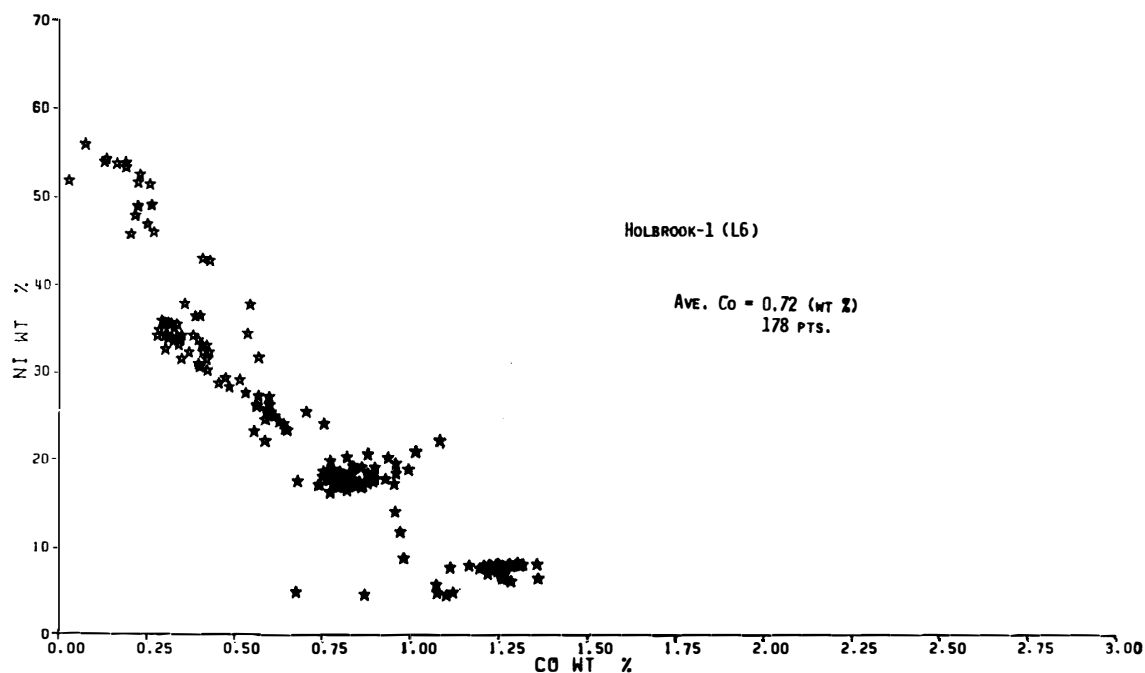


Fig. 3. Variation of Co and Ni contents of the metal phases of Holbrook-1. Overall average Co content is 0.72 wt% (178 data points).

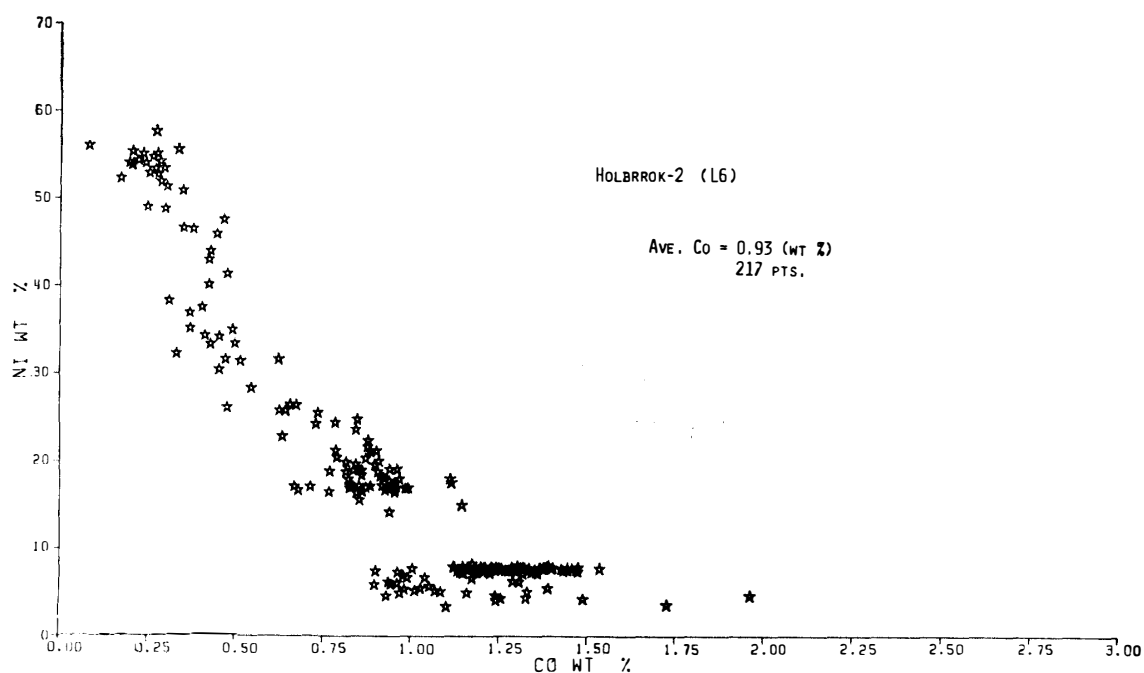


Fig. 4. Variation of Co and Ni contents of the metal phases of Holbrook-2 (L6) chondrite. Overall average Co content is 0.93 wt% (217 data points).

Holbrook consists of four fairly distinct regions of kamacite ($3 < \text{Ni} < 8$; 38.2 vol %), taenite ($25 < \text{Ni} < 47$; 22.0 vol %), Ni-rich phase I ($47 < \text{Ni} < 57$; 8.6 vol %) and an intermediate plessite phase ($11 < \text{Ni} < 24$; 31.2 vol %), as shown in Table 1 (cf. Figs.

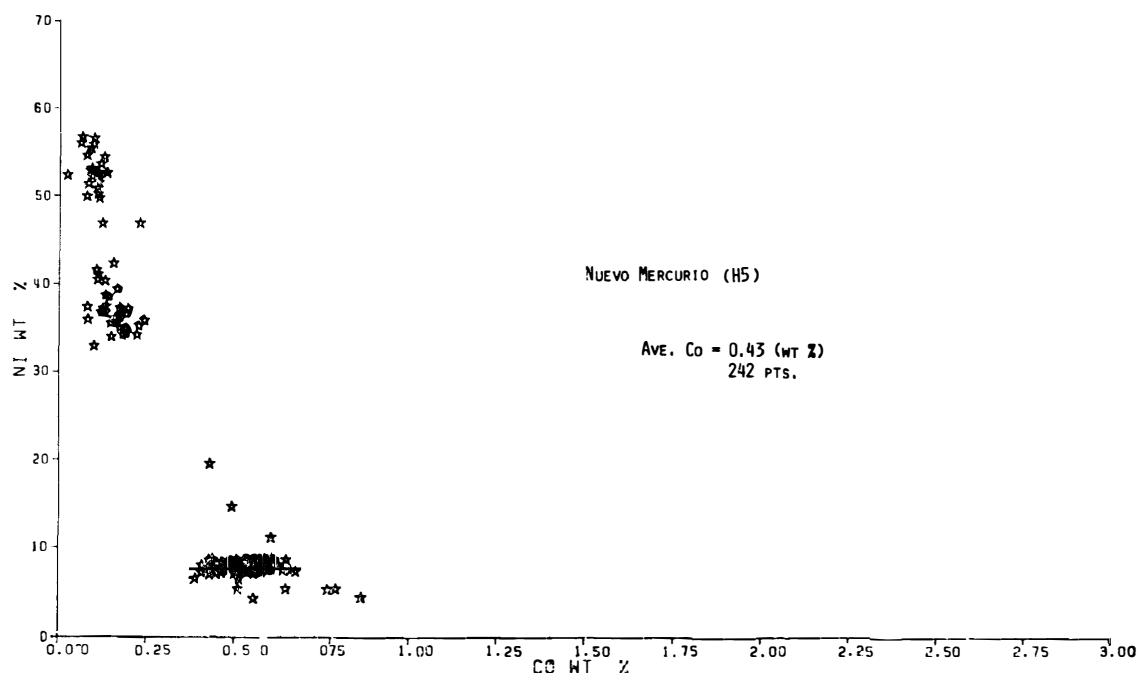


Fig. 5. Variation of Co and Ni contents of the metal phases of Nuevo Mercurio (H5) chondrite. Overall average Co content is 0.43 wt% (242 data points).

Table 1. Volume percentages of the various Ni-Fe metal regions in Holbrook-1 and -2, Nuevo Mercurio, and Allende-1 and -2 chondrites.

Sample	No. analyzed	Kamacite	Plessite	Taenite	Ni-rich phase I	Ni-rich phase II
Holbrook-1	178	24.2% [43] *	37.6% [67]	30.9% [55]	7.3% [13]	—
Holbrook-2	217	49.8% [108]	25.8% [56]	14.7% [32]	9.7% [21]	—
Holbrook (Av.)	395	38.2% [151]	31.2% [123]	22.0% [87]	8.6% [34]	—
Nuevo Mercurio	242	74.8% [181]	1.2% [3]	14.9% [36]	9.1% [22]	—
Allende-1	43	—	—	—	—	100.0% [43]
Allende-2	118	—	—	3.4% [4]	—	96.6% [114]
Allende-3	161	—	—	2.5% [4]	—	97.5% [157]

* Numbers of analytical points are shown in square brackets.

3 and 4). The composition of the Ni-rich phase I corresponds to tetrataenite (CLARK and SCOTT, 1980).

Nuevo Mercurio shows three distinct regions: kamacite ($4 < \text{Ni} < 8$; 74.8 vol %), taenite ($32 < \text{Ni} < 46$; 14.9 vol %), Ni-rich phase I ($49 < \text{Ni} < 56$; 9.1 vol %) plus, possibly, a fourth region with a small amount of a plessite phase ($11 < \text{Ni} < 18$; 1.2 vol %). The Ni-Co and Fe-Ni-Co distribution patterns in the Nuevo Mercurio chondrites are shown in Figs. 5 and 9.

Allende (CV3) displays a very distinct region of Ni-rich phase II ($67 < \text{Ni} < 72$; 97.5 vol %) with a few analytical points giving the composition of Ni-rich phase I ($43 < \text{Ni} < 44$; 2.5 vol %), as shown in Figs. 6 to 8 and Table 3. According to CLARK *et al.* (1971) the Ni-rich phase II corresponds in composition to awaruite. The extraor-

Table 2. Average compositions of the various Ni-Fe metal regions in Holbrook-1 and -2 and Nuevo Mercurio chondrite.

Sample	Content	Kamacite	Plessite	Taenite	Ni-rich phase I
Holbrook-1		[43]*	[67]	[55]	[13]
	Ni	6.80(107)**	18.21(239)	32.38(508)	52.08(263)
	Fe	92.00(114)	80.99(234)	67.22(500)	47.76(258)
Holbrook-2	Co	1.20(13)	0.80(11)	0.40(11)	0.16(7)
		[108]	[56]	[31]	[22]
	Ni	6.41(111)	17.86(217)	33.88(723)	53.30(242)
Nuevo Mercurio	Fe	92.36(118)	81.28(213)	65.64(715)	46.46(240)
	Co	1.23(17)	0.86(10)	0.48(13)	0.24(6)
		[181]	[3]	[36]	[22]
	Ni	7.27(78)	14.37(323)	36.49(342)	53.29(214)
	Fe	92.20(76)	85.14(316)	63.37(341)	46.63(214)
	Co	0.53(6)	0.49(7)	0.14(4)	0.08(3)

* Numbers of analytical points are shown in square brackets.

** Numbers in parentheses are standard deviations referring to the last decimal place.

Table 3. Average compositions of Ni-Fe metal regions in Allende chondrites.

Sample	Content	Ni-rich phase I	Ni-rich phase II
Allende-1			[42]*
	Ni	—	68.81(53)**
	Fe	—	29.54(54)
Allende-2	Co	—	1.65(12)
		[4]	[114]
	Ni	43.73(15)	69.28(74)
Allende-3	Fe	54.33(14)	29.01(71)
	Co	1.94(4)	1.71(18)
		[4]	[156]
	Ni	43.73(15)	69.16(72)
	Fe	54.33(14)	29.15(71)
	Co	1.94(4)	1.69(17)

* Numbers of analytical points are shown in square brackets.

** Numbers in parentheses are standard deviations referring to the last decimal place.

dinarily high Ni and Co contents and the virtual absence of any composition in the lower Ni and Co ranges are characteristic of Allende.

It is clear from in Tables 1 to 3 and Figs. 3, 4 and 6–8 that there is great similarity in the data obtained from two samples of Holbrook which came from randomly cut samples of different individuals of this meteorite residing in different collections in different countries. The same is true of Allende. This clearly indicates that it is possible to obtain a true representation of the Ni-Co characteristics of the metal phases of these chondrites from a single polished section. In particular, the average compositions of four Ni-Fe-Co metals are the same in both Holbrook-1 and -2 (Table 2), although the corresponding volume percentages of the four regions (in Table 1) are appreciably different from one another mainly because of inhomogeneity of the different

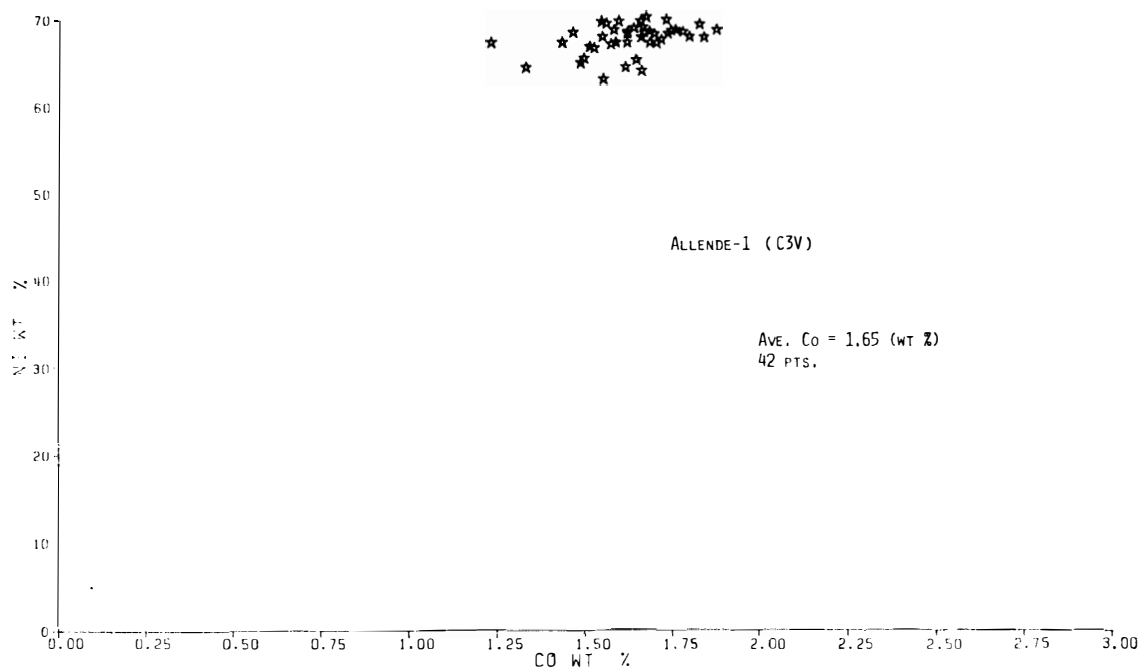


Fig. 6. Variation of Co and Ni contents of the metal phases of Allende-1 (CV3) chondrite. Overall average Co content is 1.65 wt% (42 data points).

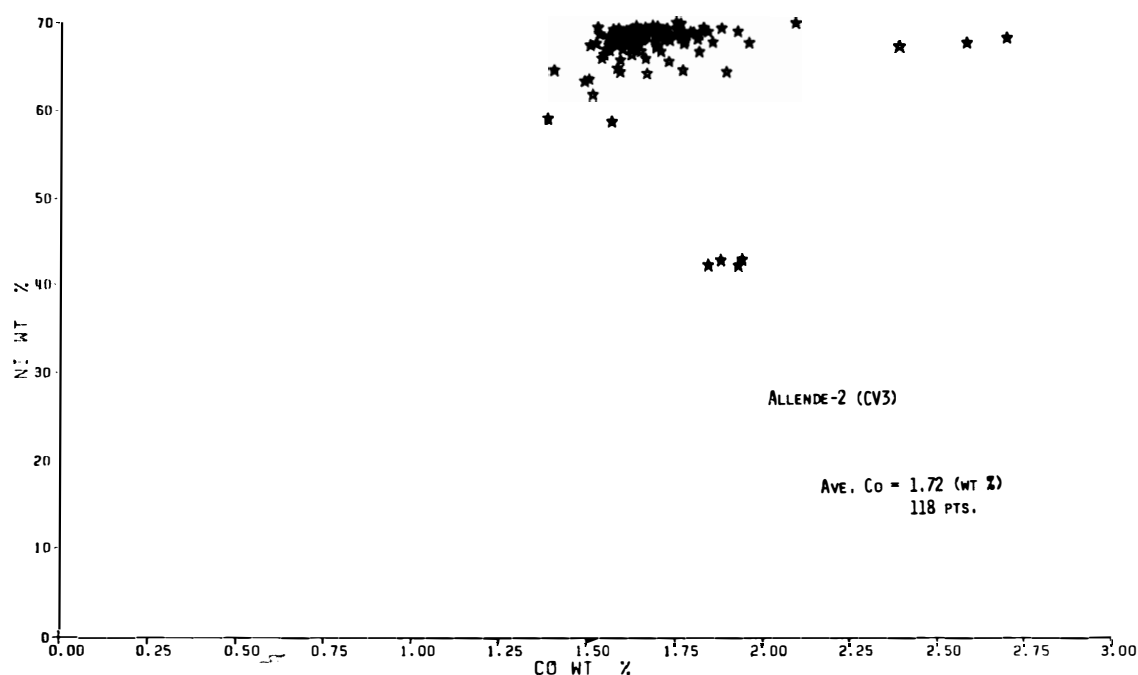


Fig. 7. Variation of Co and Ni contents of the metal phases of Allende-2 (CV3) chondrite. Overall average Co content is 1.72 wt% (118 data points).

fragments and inevitably, some operator bias in choosing analytical points.

Figure 9 shows the variation patterns for the three different chondrites obtained from data where the total weight percent $(\text{Ni} + \text{Fe} + \text{Co}) > 95$. The four phases

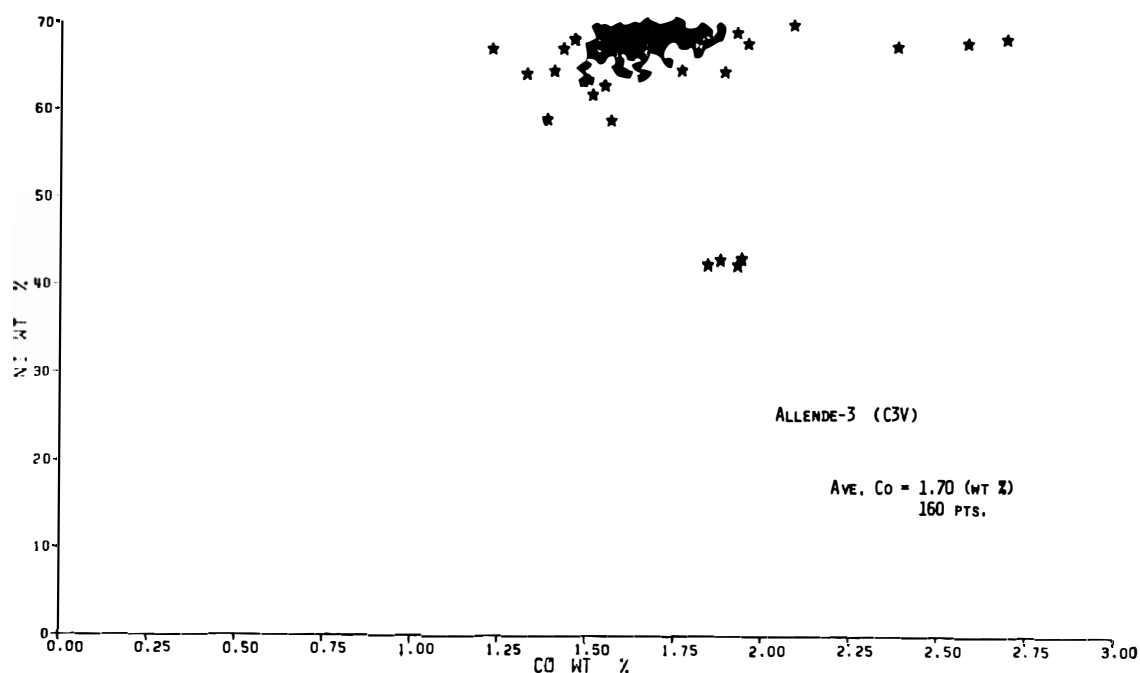


Fig. 8. Variation of Co and Ni contents of the metal phases of "Allende-3". Data points are a compilation of those of Allende-1 and -2. Overall average Co content is 1.70 wt % (160 data points).

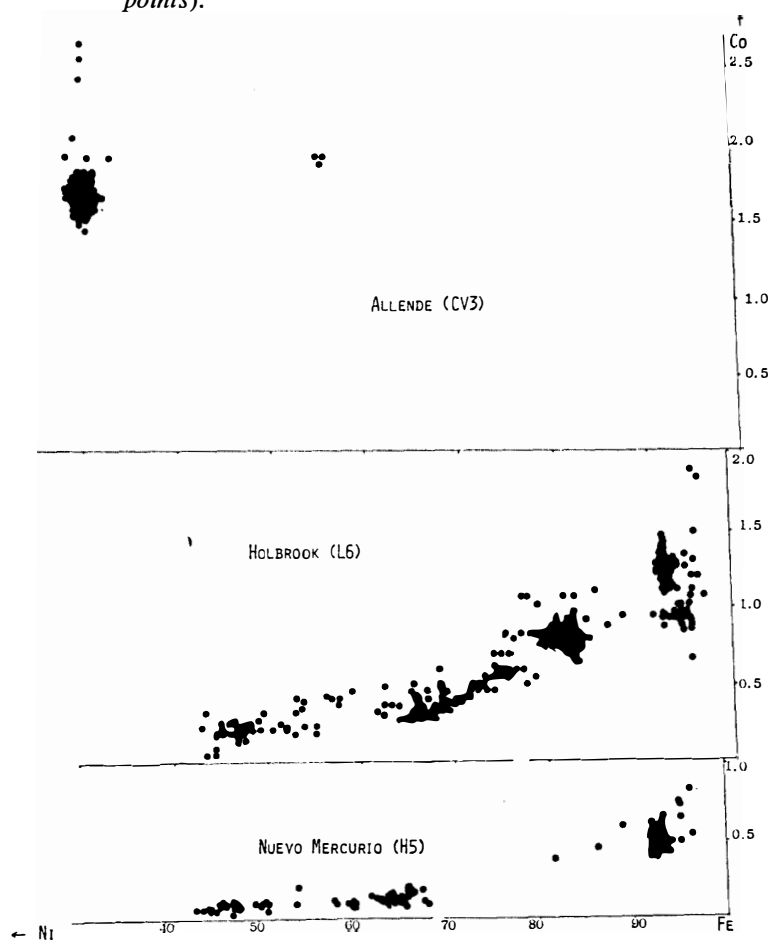


Fig. 9. Comparison of the variations of Fe, Co and Ni contents of metal phases of Holbrook, Nuevo Mercurio and Allende. Five distinct regions can be discerned. Kamacite in Holbrook spreads into both a Co-rich and a Co-poor region. Intermediate data points among the five regions may be due to intergrowths.

(kamacite, taenite, Ni-rich phases I and II) can be observed in Fig. 9; also, it is apparent that Holbrook shows fine-scale intergrowths amongst the phases, especially in the plessite region.

3.3. Co content

The Holbrook-1 and -2 gave an average Co=0.72 and 0.93 wt %, respectively, whereas Nuevo Mercurio has an average Co=0.43 wt %. The Allende-1 and -2 show extraordinarily high average Co contents of 1.65 and 1.72, respectively (Table 4). The

Table 4. Overall average compositions of Ni-Fe-Co metal grains in Holbrook, Nuevo Mercurio and Allende chondrites.

Sample	Total points analyzed	Ni (wt %)	Fe (wt %)	Co (wt %)
Holbrook-1 (L6)	178	22.31(1309)*	76.97(1277)	0.72(35)
Holbrook-2 (L6)	217	18.04(1546)	81.03(1511)	0.93(38)
Nuevo Mercurio (H5)	242	15.89(1577)	83.68(1660)	0.43(18)
Allende-1 (CV3)	42	68.81(53)	29.54(54)	1.65(12)
Allende-2 (CV3)	118	68.41(468)	29.87(463)	1.72(18)
Allende-3 (CV3)	160	68.52(403)	29.78(399)	1.70(17)

* Numbers in parentheses are standard deviations referring to the last decimal place. For example, 1309 means ± 13.09 .

overall Co and Ni contents of the Ni-Fe-Co metal phases of these chondrites plot close to the previous data by LOVERING (1964) and SMITH and STEELE (1976), especially in the case of Holbrook and Allende.

AFIATTALAB and WASSON (1980) and SEARS and AXON (1976) have reported that the Co contents of kamacites in ordinary chondrites show non-overlapping ranges, *i.e.*, H group=0.33–0.44 wt % Co, L group=0.67–0.82 wt % Co and LL group=1.5–11 wt % Co. The Co contents reported here for five samples, plus the six chondrites reported by SMITH (1980) and two chondrites by SMITH and LAUNSPACH (1983), do not substantiate such a simple and straightforward pattern of variation. Thus the kamacites in Holbrook-1 and -2 contain 1.20 and 1.23 wt % Co, while the kamacite in Nuevo Mercurio contains only 0.53 wt % Co (Table 2). Thus the Co contents of kamacite in these chondrites are inconsistent with those obtained by AFIATTALAB and WASSON (1980), although the general tendency of Co in the kamacites to increase from H through L to LL groups is supported by this study. The variation patterns of the Ni-Co metal phases shown in Figs. 3–8 and Fig. 4 in SMITH (1980), and Fig. 1 in SMITH and LAUNSPACH (1983) indicates that, except for Ni phase II, there is a clear trend in Co concentration with low Co being associated with high Ni, and high Co with low Ni and high Fe.

In the kamacite of Holbrook, two different average compositions can perhaps be discerned as follows (Fig. 9):

- 1) Co-poor region: Ni 5.61 (128) Fe 93.39(131) Co 1.00(10).
- 2) Co-rich region: Ni 6.78(96) Fe 91.94(92) Co 1.28(11).

These two different Co concentrations may either be representative of (1) two different

generations of kamacite—*i.e.*, kamacite formed at significantly different times and temperatures in the thermal history of this chondrite; or (2) mixing with material with the characteristics of petrologic type 5. The latter possibility could be investigated by using statistical analysis of textural characteristics and electron microprobe analyses of the constituent minerals in Holbrook-1 chondrite as L5 (55%) (*cf.* MIÚRA and MATSUMOTO, 1982).

3.4. Formation process

Table 5 shows concentration characteristics of the data points and abundance characteristics of metal regions, together with the previous data by SMITH (1980) and SMITH and LAUNSPACH (1983). Two H5 chondrites show the similar variation patterns with little or no plessite. But six L6 chondrites show very significant differences between the average metal compositions and the concentration and abundance characteristics of the Ni-Fe-Co patterns.

Table 5. Concentration characteristics of data points and abundance characteristics of metal regions in chondrites investigated.

Group and type	Sample locality	Concentration characteristics of data points	Abundance characteristics of metal regions
L4	Mossgiel*	Distinct	Ni-I \gg T \geq K > P*
L5	Timmersoi*	Diffuse	P \gg T > K
L6	Holbrook	Diffuse	K > P > T \gg Ni-I
	Bruderheim*	Fairly diffuse	P > T > K > Ni-I
	Catherwood*	Diffuse	K \gg T > P \geq Ni-I
	Artracoona*	Diffuse	P \gg T \geq K \gg Ni-I
	Peace River**	Diffuse	K > T \gg Ni-I > P
	L'aigle**	Fairly diffuse	K \gg T \geq P \geq Ni-I
L5-6	Vilna*	Very diffuse	K \gg P \geq T > Ni-I
LL5-6	Innisfree*	Random	T > K \geq Ni-I > P
H5	Kielpa*	Distinct	K \gg T \geq Ni-I \gg P
	Nuevo Mercurio	Distinct	K \gg T \geq Ni-I \gg P
CV3	Allende	Sharp	Ni-II \gg Ni-I

* Data reported by SMITH (1980).

** Data reported by SMITH and LAUNSPACH (1983).

* K: Kamacite, P: Plessite, T: Taenite, Ni-I: Ni-rich phase I, Ni-II: Ni-rich phase II.

The great differences in the variation patterns of Ni-Fe and Ni-Co from one chondrite to another, even with the same group and petrologic type, as well as the differences in the average Ni and Co contents of the metal phases, suggests a convenient method for "fingerprinting" chondrites.

It seems likely that the Fe, Ni and Co variations in each of these chondrites are not directly related to the events that produced the different groups (H, L, LL, etc.), but rather to processes of planetary accretion and low temperature burial metamorphism. If this is the case, they have the potential of revealing important information about accretion histories and the later thermal events affecting these meteorites. Clearly, many more data are desirable from a wide range of chondrites, such as the Antarctic meteorites reported by MIÚRA and MATSUMOTO (1982).

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