ABSTRACT

THE PREFERENTIAL ACCEPTANCE OF CERTAIN IONS INTO THE FERRITE SPINEL LATTICE

by Allen Vaughan Shaw

It is well known that minerals of the spinel group crystallize with a variety of chemical formulas and that solid solution occurs freely among members of the various spinels series. Little work has been done, however, concerning preferential acceptance of ions into the spinel lattice.

To fill this area to some degree, several members of the ferrite series of spinels were synthesized by heating mixtures of coprecipitated hydroxides to temperatures of 600° to 1000° C. and held there for not less than 12 hours. X-ray diffraction analysis showed that the order of acceptance at these temperatures and at one atmosphere of pressure was

Zn, Mg, Ni, Cu, and Mn.

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It is concluded that the primary control of the acceptance is the electron configuration of the element and not the ionic radius or ionization potential. These conclusions may be affected by an increase in temperature, pressure, or available constituents.

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By

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INTRODUCTION

Geochemists have long studied various chemical systems in an attempt to develop theories concerning the crystallization of the rock forming minerals and the geochemical distribution of the elements. Washington and Clark (1924) determined that eight elements (O, Si, Al, Fe, Ca, Na, K, and Mg) were the most abundant in the earth's crust. These are termed the common elements by Rankama and Sahama (1950) and the remainder as trace elements. How these elements are distributed in the rocks and minerals of the earth is determined by a number of variables such as valence, ionization potential and ionic radius. In the following pages, a series of spinels of the ferrite group has been studied in the hope that some additional information might be gleaned concerning the function of these variables.

Review of Spinels

Minerals of the spiral type are among the earliest minerals to crystalize from a magma. Bowen (1926) places them just below the olivines in his reaction series, but from the interstitial occurrence of these minerals, it appears that they may continue to crystallize throughout the crystallization history of the magma. Spinels are quite ubiquitous, being found as accessories in metamorphic and igneous rocks and as heavy minerals in clastic sediments (Deer *et al*., 1963).

Palache *et al*. (1944) divide the spinel group of minerals into three isomorphic series based on the dominant trivalent ion; these are the aluminates, the magnetites, and the chromites. Two other geologically important minerals within this structure type are maghemite (γ - hematite) and ulvospinel, the latter being a titaniferous variety. Table 1 illustrates the various spinel series as found by Goodenough and Loeb (1955).

TABLE 1.--(N) indicates normal structure is inferred, the cation distribution not experimentally established. Distributions marked with asterisks are not entirely inverse; the number of divalent ions in the tetrahedral sites as temperature dependent. The letters N and I refer to normal and inverse spinel structure.

	Y^{3+} or Z^{4+}											
X^{2+}	Al^{3+}	V^{3+}	Cr^{3+}	(Mn^{3+})	Fe^{3+}	Rh^{3+}	Ga^{3+}	In^{3+}	Ge^{4+}	Sn^{4+}	Ti^{4+}	V^{4+}
Mg	N	N	N		I*	N	I*	I*			I	I
Mn	N	N	N	(N)	I							
Fe	N	N	N		I							
Co	N		N		I				N	I	I	
Ni	¼N3/4I		N		I				N			
Cu	(N)		I		I*							
Zn	N	N	N	(N)	N	N	(N)			I	I	
Cd	N		N		N		N		(N)			

(Goodenough and Loeb, 1955)

As might be expected from the above, spinels are able to accept a wide variety of elements into their lattice without major structural variations. Gorter (1954) lists twenty-two different elements as being found in spinels (Table 2).

TABLE 2.--Elements found in minerals with a spinel-type structure, listed by valences. After Gorter (1954) and Ringwood (1959).

Univalent:	H, Li, Cu, Ag, Na
Divalent:	Mg, Ca, Mn, Fe, Co, Cu, Zn, Cd
Trivalent:	Al, Ti, V, Cr, Mn, Fe, Ga, Rh, In
Tetravelent:	Ti, V Mn, Ge, Sn, Mo, W

The spinel structure was first determined by two independent workers, Bragg and Nishikawa, in 1915. Through x-ray diffraction methods, they found that the oxygen atoms were in approximate cubic closest packing (Fig. 1) and that the general formula was AB_2O_4 (Bragg, 1915). The ions in position A were divalent and in four-fold coordination with oxygen, while those ions in the B positions were trivalent and in six-fold coordination (Fig. 2). Subsequently, Barth and Posnjak (1931) discovered a second spinel structural type with the general formula $B(AB)O_4$. In this form, the A ion

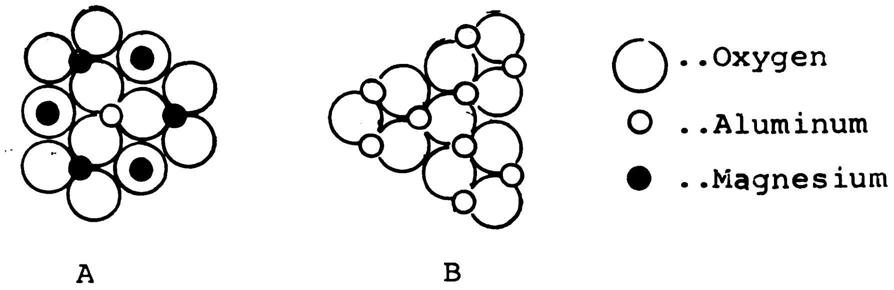

Fig. 1.--Successive layers in the spinel structure showing the packing of the ions. (a) is the lowermost layer. After Bragg (1937).

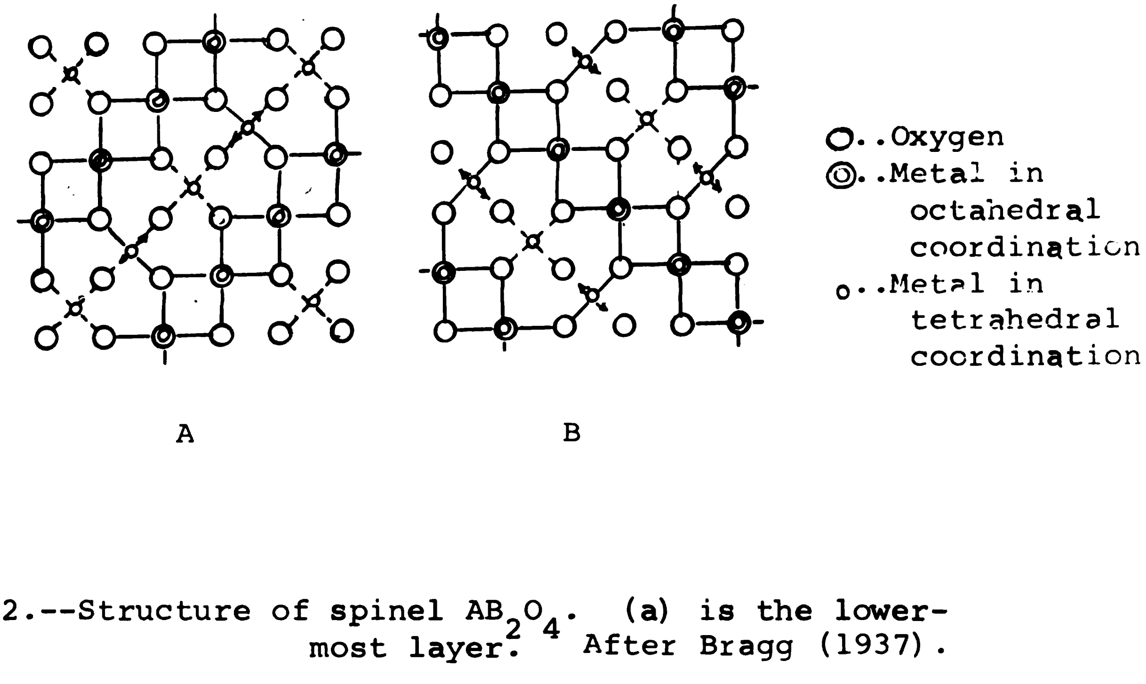

Fig. 2.--Structure of spinel AB_2O_4. (a) is the lowermost layer. After Bragg (1937).

is in octahedral coordination, as is one of the B ions, with oxygen, while the other B ion is in tetrahedral coordination. This lattice is said to have "variate atom equipoints" meaning that similar ions can be found in two different structural positions within the lattice.

Table 1 shows that the majority of spinels are normal in structure and only the ferrites are commonly inverse. A great deal of work has been done in an attempt to explain the cause of the inverse structure which Goodenough and Loeb (1955) have approached from a theory of covalent bonding, Gorter (1954) has attacked from a consideration of the electron configuration of the ions, while Verwey and Heilman (1947) simply state that trivalent and tetravalent ions occupy the octahedral sites preferentially, with the exception of Fe, In, and Co which also occupy tetrahedral positions.

Of the spinels, the ferrites have been studied most extensively, however in recent years interest has been shown in the entire series. In spite of this, little has been done concerning preferential composition of the minerals and it is hoped that the present work will contribute some knowledge of this area.

THEORY

The ability of one element to substitute for another is well known to mineralogists and petrologists. If an element substitutes for another in the same structural position, the substitution is termed disdochic. Isomorphism is defined as the ability of two compounds of similar structural type to incorporate more than 5 percent of each other in solid solution (Rankama & Sahama, 1950; Wells, 1962). The spinels are an isomorphous mineral group, with diadochic substitution occurring among the elements listed in Table 2.

Goldschmidt (1937) was the first to offer a theory concerning geochemical distribution of the elements. On the assumption that ionic bonding is the dominant bond type in the majority of rock forming minerals, he postulated the following rules:

1. For two ions to substitute diadochically one for another in a crystal structure, the ionic radii must not differ by more than 15 percent.

2. When two ions possessing the same charge, but different radii, compete for a position in the crystal structure, the ion with the smaller radius is preferred.
3. Ions having similar radii, but different charges of the same sign may substitute diadochically in a crystal; in which case, the ion having the larger charge has preference over the ion with the lesser charge.

In 1951, Fyfe pointed out that mineral bonds are not completely ionic and suggested that the following criteria be used when discussing diadochic substitutions:

1. Two ions will substitute for one another if their sizes are similar.
2. Two ions will substitute for one another if the number and directional properties of the bonds are similar.
3. Two ions will substitute for one another if the bond types are similar.

Thus, although the first of Fyfe's rules is similar to Goldschmidt's, a consideration of the electron configuration and tendency of coordination is added.

Ahrens (1953) uses the ionization potential of an element as a key to its distributional tendencies. He states that when two ions of the same valence and similar radii compete for a structural site, the one with the greater ionization potential should arrive first, but may not remain at that site. The ability to remain at a site depends on the bond stability of the anion and the directional properties of the cation toward the anion.

Ringwood (1955a,b) states:

> 1. Whenever diadochy in a crystal is possible between two elements possessing appreciably different electronegativities, the element with the smaller electronegativity is preferentially incorporated.
>
> 2. When diadochy occurs between elements possessing similar electronegativities, the Goldschmidt Rules are usually applicable.

Table 3 lists the elements used in this investigation, their radii, ionization potentials and electronegativity. Note the correlation between the latter two qualities, from which one may conclude that Ringwood simply restates Ahrens' results. The elements chosen for this study show varying degrees of natural association and diadochy. With the exception of magnesium, they are all members of the first transition series. Table 4 shows the electron configuration of the elements considered.

TABLE 3.--All data except electronegativity after Green, 1959. Electronegativity after Ringwood, 1955. Asterisk indicates radii in four-fold coordination; all others in six-fold.

Ion	Ionic Radius	Ionization Potential v.	Electronegativity
Cu	.96	7.223	1.8
Cu	.72	20.28	2.0
Mg	.66	14.97	1.2
Ni	.69	18.13	1.7
Zn	.71*/.74	17.89	1.7
Fe	.74	16.24	1.65
Fe	.64	-	1.8
Mn	.80	15.70	-
Mn	.66	32.00?	-
Mn	.57*/.60	52.00?	-

TABLE 4.--After Rankama & Sahama, 1950 Electron configuration of the elements.

Shell	1	2		3			4				5				6		
Group	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6p	6d	6f
Element																	
Mg	2	2	6	2													
Mn	2	2	6	2	6	5	2										
Fe	2	2	6	2	6	6	2										
Ni	2	2	6	2	6	8	2										
Cu	2	2	6	2	6	10	1										
Zn	2	2	6	2	6	10	2										
Cd	2	2	6	2	6	10	2	6	10		2						
Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2		

Copper is classified as a chalcophile element, meaning that it occurs as a sulfide more commonly than as an oxide (lithophile) or as a free metal (siderophile). Unlike the elements which directly precede it in the periodic table, copper oxide (CuO) forms a structure where the metal is in tetrahedral coordination with oxygen, while the monoxides of Mn, Fe, Co, and Ni have the NaCl type of structure where the metal is in octahedral coordination. Zinc, the other chalcophile element studied, forms simple oxides with a wurtzite structure, where the metal is in four-fold coordination with oxygen.

Iron and nickel are siderophile elements, while manganese and magnesium are classified as lithophile. Magnesium, however, often diadochically substitutes for iron, as does nickel; and both iron and nickel readily form sulfides and iron oxides. It does not seem likely that these classifications would indicate a preference in the present study.

Predictions

According to Wells (1962, p472) all manganese hydroxides form Mn_3O_4 when heated above 1000° C. Since this is the upper limit of the experimental temperatures used in this investigation, one might expect to find this form of manganese as a product. This structure might also be expected to accommodate other elements; therefore a general formula might be AMn_2O_4.

There are a number of possible products which could be derived from these reactants. Since hydroxides change to oxides when heated, it is possible that a mixture of simple oxides might be found. A second possibility is that a complex oxide (ferrite) plus a simple oxide will be formed. These are the desired products. A third possibility might be a complex oxide of the general formula $(A,B)Fe_2O_4$, where A and B are the two divalent elements present in the reactants, and two simple oxides, AO and BO, composed of the ions which did not enter the ferrite lattice.

Half of the elements used in these experiments have only one oxidation state and are divalent. Fe, Cu, and Mn can have several valencies. Heslop and Robinson (1960) state that tenorite (CuO) goes to cuprite (Cu_2O) at 900° C., but is stable at normal temperatures. Thus, at the upper limit of the temperatures involved, copper would not have a valence that would allow the formation of a copper ferrite.

On the basis of ionic radii, the expected order of substitution is:

Mg, Ni, Zn, Cu, Mn.

Thus, no manganese ferrite should be formed except as a control, copper ferrite only when paired with manganese, etc. If Ahrens' theory is used, the order is:

Cu, Ni, Zn, Mn, Mg.

It is easily seen that nickel and zinc retain their positions, while copper becomes more favored and magnesium less so. Thus nickel ferrite should be formed in preference to that of zinc and zinc ferrite in preference to that of manganese. This is in keeping with the findings of Wager and Mitchell (1951) in their studies of the Skaergaard intrusion.

EXPERIMENTAL PROCEDURE

There are several methods of synthesizing spinel-type minerals. Spiroff (1938) precipitated magnetite by slowly dripping ferric sulfate and ferrous chloride into a weak ammonia solution. Posnjak (1930) formed zinc ferrite by heating equal parts of zinc carbonate and ferrous oxide together. Mason (1947) created both manganese and zinc ferrites by heating a precipated mixture of hydroxides. The latter method is the one followed in this work.

The original chemicals (Baker Reagent grade) were the sulfates of the desired elements. Since Mason was not specific in his description of technique, the individual sulfates were tested with each of the precipitating agents (NaOH and Na_2CO_3) to determine any variation in reactions. There was none.

The sulfates desired for a particular mixture were weighed on a rough balance to get approximate amounts and then were transferred to Chain-o-matic balance for accurate measurements. The quantitites were calculated to give a ration of one mole of divalent ion to two moles of trivalent ion. The sulfates were then added to enough boiling deionized water to make a .25 N solution. The solution was stirred until all of the sulfate had dissolved, then 250 mls. of .5 N sodium carbonate solution and an equal amount of 1 N sodium hydroxide solution were added to precipitate the mixed hydroxides according to the following equation: $2BSO_4 + 2ASO_4 + 2Na_2CO_3 + 4NaOH \rightarrow 2A(OH)_2 + 2B(OH)_2 + 4Na_2SO_4 + 2CO_2$. The precipitate was usually dark in color and curdy in appearance. The mixture was stirred to insure completing the reaction and allowed to settle. A few drops of sodium carbonate solution were added to check the completeness of the reaction. If complete, the beaker was set aside to cool, if the reaction was incomplete, more of the precipitating agents were added, the mixture again stirred and tested.

As soon as the precipitate had settled after a completion of the reaction, the residual fluid was decanted and the precipitate washed by adding deionized water and stirring the mixture, followed by a period of settling and decanting the wash water. This procedure was repeated several times and then a test for sulfate was made in the following manner:

Two milliliters of the wash water were placed in a test tube and tested for extremes of pH with litmus paper. If highly acid or base, it was neutralized by adding ammonium hydroxide or hydrochloric acid. Then .5 milliliters of 5N hydrochloric acid were added followed by .5 milliliters of barium chloride solution. If any sulfate ion was present, a fine white precipitate of Ba_2SO_4 formed (See McAlpine and Soule, 1949, p. 215).

When a negative sulfate test had been obtained, the precipitate was placed in a Bucher funnel and at least one liter of deionized water filtered through it. A final sulfate test was run and the solid placed in a covered beaker in a drying oven for a period of twelve hours. The dried solid was crushed and portions of not less than a gram were weighed out. These were placed in high alumina crucibles (Made by Norton and purchased from the Fisher Company) which were then placed in an electric furnace and heated to the desired temperature. This temperature was held for twelve or sixteen hours after which the crucibles were removed and allowed to cool. Since the transition of spinels from a high temperature is slow, no attempt was made to quench the products other than to leave them at room temperature.

The cooled sample was ground under acetone in an agate morter to a fine powder and mounted on a fine glass rod using clear nail polish as a mounting medium. This method was chosen over other possibilities because it seemed the quickest, easiest, and had given good results in the past. The mounts were placed in a standard Norelco powder camera and exposed for 2.6 hours to iron radiation. The films were developed in standard fashion and measured on a standard Norelco film-measuring device. For a review of x-ray procedures, see Azaroff and Buerger (1958). No attempt was made to correct for film shrinkage. The d-spacings were calculated on the CDC 3600 computer using the program appearing in Appendix 1. This method was chosen primarily for its speed (one line took less than a minute to put on a data card). The d-spacings were then compared with those recorded in the ASTM X-ray Powder Data File.

DATA

The x-ray data is presented as visually estimated line intensities and the calculated d-spacings for each film. As each mixture was heated at four different periods, there are four films in a set and these are grouped with the control binary ferrites that have been treated in a similar fashion. Thus in Table 5, Set 5.1, the data in the left hand column is that of the control copper ferrite, that in the middle column is the ternary sample (Cu, Mg) and that in the right hand column is data for magnesioferrite all heated at 1000° C. for 16 hours.

In correlating lines of each film, allowances had to be made for errors in measuring and in estimating intensities. Therefore, if two lines had similar intensities and differed by .01 Angstroms they were correlated. In some cases, the trimetallic line fell between the dimetallic controls in value, so there might be .02 difference from the high line to the low value. In those cases where the trimetallic line was within .005 of one dimetallic control and .009 of the other, the correlation was with the closest lines.

As expected, the lines recorded in the ASTM powder data files for copper ferrite do not correlate with those found in the experimental control sample in Set 5.1. However, the experimental lines do not match those recorded for the expected copper oxide (Cu_2O) either, but there is a close correlation with the ASTM lines for magnetite. With the exception of metallic copper, none of the lines listed for possible copper products in the ASTM files can be found in Set 5.1. The line superscripted 1, is the most intense line of metallic copper. Spectrochemical analysis shows that copper is indeed present, so the only conclusion is that copper exists as a metal, rather than an oxide under the conditions found in this experiment.

The copper-iron product of the control sample in Set 5.2 is similar to that found in the preceding set, but Set 5.3 has lines corresponding to the ASTM copper ferrite lines. In Set 5.4, some hematite lines are found as well as some for tenorite (CuO) anc copper ferrite.

The magnesioferrite sample in Set 5.1 has close correlation with the lines in the ASTM file. There is also a good match for magnetite, but since there is no evidence of metallic magnesium, it is felt that magnesioferrite is formed. A similar set of lines is found in Set 5.2 while at the lower temperatures of sets 5.3 and 5.4, some hematite lines and one or two weak lines which could be MgO are also found.

The Cu, Mg sample in Set 5.1 has lines which have a strong correlation with both control samples, with the exception of the third line which is superscripted 4. Although the d-spacing is .02 Angstroms shorter than that of the strongest line for Cu_2O (cuprite), this line is considered as indicating the presence of this mineral. This conclusion is supported by the presence of lines which are definitely cuprite in Set 5.2. In sets 5.3 and 5.4, the copper oxide is tenortie as expected. Hematite is found in Set 5.4 in addition. The presence of magnesioferrite is found in all samples.

TABLE 5.--Data from the ternary sample Cu,Mg,Fe compared with the binary samples Cu,Fe and Mg,Fe. [1]indicates metallic copper, [2]hemetite, [3]magnesium oxide, [4]cuprite, and [5]tenorite.

Cu,Fe		Cu,Mg,Fe		Mg,Fe		Cu,Fe		Cu,Mg,Fe		Mg,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
5	4.833							5	4.823		
20	2.962					5	4.762				
		20	2.944	40	2.933			10	2.957		
100	2.527	100	2.518	100	2.510	20	2.942			60	2.949
		5	2.451^{4}			100	2.515	100	2.526	100	2.518
3	2.424							10	2.464^{4}		
20	2.097^{1}	20	2.088	40	2.084	3	2.411	2	2.418		
10	1.716	10	1.708	30	1.708			3	2.133^{4}		
60	1.616	80	1.612	80	1.611	20	2.085^{1}	20	2.096	50	2.092
60	1.486	90	1.482	90	1.480	10	1.708	10	1.714	20	1.710
						80	1.611	80	1.616	80	1.614
								3	1.510^{4}		
						90	1.481	90	1.486	90	1.483
						5	1.416				
Set 5.1		16 hrs @ 1000° C.				Set 5.2		12 hrs @ 1000° C.			

Cu,Fe		Cu,Mg,Fe		Mg,Fe		Cu,Fe		Cu,Mg,Fe		Mg,Fe	
				5	4.807	3	4.007	3	4.818		
15	4.762									3	4.732
20	2.958	30	2.947	30	2.951	3	3.659				
				3	2.7					3	3.599
				3	2.683	3	2.953	10	2.945	20	2.936
20	2.554					40	2.684			5	2.680^{2}
		100	2.513^{5}	100	2.519	100	2.511^{5}	100	2.515^{5}	100	2.505^{2}
100	2.493^{3}					3	2.415				
10	2.410			3	2.421	40	2.317^{5}	20	2.311^{5}		
5	2.302	30	2.306^{5}							3	2.271
5	2.135^{2}					10	2.202				
		30	2.092	30	2.093			20	2.091^{3}	30	2.086^{3}
20	2.067					10	2.056				
		10	1.861	3	1.891	3	1.860	5	1.862		
3	1.731					15	1.838			5	1.835
				20	1.712			5	1.702	5	1.708
10	1.699			3	1.682	30	1.691			5	1.690^{2}
5	1.646							20	1.611	30	1.609
20	1.612	70	1.612	50	1.613			3	1.505		
20	1.595					40	1.487	95	1.481	100	1.480
		5	1.503			40	1.454			5	1.452
100	1.490^{3}	90	1.483	100	1.484						
20	1.465										
				3	1.454						
Set 5.3		12 hrs @ 800° C.				Set 5.4		12 hrs @ 600°C.			

The manganese ferrite in Set 6.1 appears to be magnetite with no evidence of manganese. Lines for the expected hausmannite (Mn_3O_4) are not present, neither are lines for any of the manganese oxides nor metallic manganese. Some manganese products have strong lines with d-spacings similar to those of magnetite, but the correlation is not line for line, and there are no extraneous lines present in the set under consideration. Spectro-chemical analysis shows the presence of manganese so one might conclude that the element is present in either an amorphous state or has substituted for iron in some fashion.

In subsequent manganese-iron samples, the product is bixbyite (Mn,Fe_2O_3) accompanied by hematite in the lower temperature ranges. The lines of the Cu,Mn sample in Set 6.1 correlate well with those of the Manganese control. There is however no evidence of either copper or manganese products even though analysis shows that both elements are present. In set 6.2 there is no correlation with either of the controls, nor with any of the ASTM lines for the expected oxides. The lines are slightly low for magnetitie, but correlate to some degree with those for maghemite. Set 6.3 has some lines which are correlatable with those recorded for copper ferrite, but there is not enough evidence to warrant calling this product copper ferrite. There is a similar situation in Set 6.4, with the exception of some lines which are definitely those of hematite. Some of the lines could be due to gamma manganese oxide, but there is no conclusive evidence for this.

TABLE 6.--Data from the ternary sample Cu, Mn, Fe compared with the binary sample Cu, Fe and Mn, Fe.

Cu,Fe		Cu,Mn,Fe		Mn,Fe		Cu,Fe		Cu,Mn,Fe		Mn,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
		20	4.869					10	4.787		
5	4.833					5	4.762				
		20	2.983	10	2.972					20	3.824
20	2.962									20	3.656
		100	2.546	100	2.538			20	2.958		
100	2.527					20	2.942				
3	2.424	5	2.438							100	2.703
		20	2.112	30	2.109			100	2.531		
20	2.097					100	2.515			30	2.509
		10	1.729	20	1.727			10	2.424		
10	1.716					3	2.411				
		70	1.630	100	1.627					30	2.347
60	1.616									20	2.205
		70	1.498	100	1.497			45	2.103		
60	1.486					20	2.085				
										30	2.004
										60	1.842
								30	1.723		
						10	1.708				
										40	1.693
										80	1.664
								85	1.643		
						80	1.611				
										5	1.526
						90	1.481	90	1.493	5	1.488
										10	1.453
						5	1.416			60	1.424
Set 6.1		16 hrs @ 1000° C.				Set 6.2		1000° C.			
15	4.762					3	4.807				
				7	3.8			5	4.747		

TABLE 6.--Data from the ternary sample Cu, Mn, Fe compared with the binary sample Cu, Fe and Mn, Fe.

Cu,Fe		Cu,Mn,Fe		Mn,Fe		Cu,Fe		Cu,Mn,Fe		Mn,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
		20	4.869					10	4.787		
5	4.833					5	4.762				
		20	2.983	10	2.972					20	3.824
20	2.962									20	3.656
		100	2.546	100	2.538			20	2.958		
100	2.527					20	2.942				
3	2.424	5	2.438							100	2.703
		20	2.112	30	2.109			100	2.531		
20	2.097					100	2.515			30	2.509
		10	1.729	20	1.727			10	2.424		
10	1.716					3	2.411				
		70	1.630	100	1.627					30	2.347
60	1.616									20	2.205
		70	1.498	100	1.497			45	2.103		
60	1.486					20	2.085				
										30	2.004
										60	1.842
								30	1.723		
						10	1.708				
										40	1.693
										80	1.664
								85	1.643		
						80	1.611				
										5	1.526
						90	1.481	90	1.493	5	1.488
										10	1.453
						5	1.416			60	1.424
Set 6.1		16 hrs @ 1000° C.				Set 6.2		1000° C.			
15	4.762					3	4.807				
				7	3.8			5	4.747		
				10	3.633			3	3.805		
20	2.958	20	2.945			3	3.659				
				100	2.697			5	3.636	3	3.633
20	2.554					3	2.953				
		100	2.521					50	2.901		
100	2.493			10	2.500			80	2.680	100	2.689
10	2.410	10	2.415			100	2.511	100	2.505	50	2.498
				10	2.340	3	2.415	5	2.412		
5	2.302							5	2.340		
				10	2.201	40	2.317				
5	2.135					10	2.202	10	2.196	20	2.195
		45	2.094					10	2.084		
20	2.067					10	2.056				
				10	1.999			3	1.995	3	1.999
				20	1.839	3	1.860				
3	1.731					15	1.838	20	1.833	50	1.835
		30	1.714	5	1.715			5	1.720		
				10	1.689	30	1.691	20	1.689	50	1.690
				80	1.659			10	1.656	40	1.659
5	1.612	90	1.616					20	1.609		
				7	1.525					3	1.597
100	1.490	100	1.485	20	1.486					3	1.522
20	1.465					40	1.487	80	1.482	40	1.485
				50	1.453	40	1.454	20	1.451	50	1.452
Set 6.3		12 hrs @ 800° C.				Set 6.4		12 hrs. @ 600° C.			

The strongest line in the nickel control sample of Set 7.1 is a little shorter than the ASTM record d-value for nickel ferrite, but the remaining lines are quite accurate and the material is undoubtedly nickel ferrite. The lines in the subsequent sets are also quite close to the recorded values for the ferrite. One deviation from previous samples is the absence of hematite in the lower temperature ranges. The d-spacings are quite consistent for the most part, indicating that nickel ferrite is easily formed at all temperatures encountered in this research.

The Cu,Ni sample in Set 7.1 is rather inconclusive as there is no evidence of copper. The strong lines are those of nickel ferrite. The absence of copper ferrite, copper oxides, and metallic copper offers rather negative evidence for the formation of nickel ferrite in preference to copper ferrite. In Set 7.2, there is also good correlation with the nickel ferrite control, and no evidence of copper. It is possible that the line 2.304, superscripted 1, represents tenorite as it is only .02 Angstroms away from a strong tenorite line and does not correlate with any of the nickel ferrite lines. If this is true, then another strong line can be found in 2.501 which is also .02 Angstroms away from the ASTM line, but occurs in the nickel ferrite values also.

In Set 7.3, the tenorite lines are much more plausible as 2.314 is quite strong and does not correlate with either of the control samples. Again there is a strong correlation between the nickel ferrite control and the ternary sample, especially in the lower d-spacings, Set 7.4 continues this trend with both tenorite and nickel ferrite lines and no apparent hematite.

TABLE 7.--Data from the ternary sample Cu,Ni,Fe compared with the binary sample Cu,Fe and Ni,Fe. ^{1}indicates CuO.

Cu,Fe		Cu,Ni,Fe		Ni,Fe		Cu,Fe		Cu,Ni,Fe		Ni,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
5	4.833									5	4.797
		20	4.762			5	4.762	3	4.752		
20	2.962									30	2.966
		30	2.925			20	2.942	20	2.931		
				5	2.891	100	2.515				
100	2.527							100	2.501	100	2.506
		100	2.502	100	2.491	3	2.411				
3	2.424							5	2.390	5	2.398
		3	2.397					15	2.304		
20	2.097					30	2.085			30	2.079
				10	2.072					3	1.997
		3	1.912			10	1.708	80	1.700	10	1.700
		3	1.766			80	1.611	80	1.604	70	1.603
10	1.716					90	1.481	90	1.474	80	1.474
		10	1.700	10	1.697	5	1.416			5	1.408
60	1.616										
		85	1.603	60	1.601						
60	1.486										
		90	1.474	60	1.472						
		5	1.411								
Set 7.1		16 hrs @ 1000° C.				Set 7.2		12 hrs @ 1000° C.			
15	4.762					3	4.807				
20	2.958							5	4.732		
		5	2.933			3	3.659				
				5	2.918	3	2.953				
20	2.554							10	2.929	5	2.927
100	2.493	100	2.503	90	2.493			2	2.739		
10	2.410	5	2.409			100	2.511	100	2.500	40	2.492
				5	2.394	3	2.415				
		40	2.314					7	2.394	3	2.396
5	2.302					40	2.317				
5	2.135							15	2.304		
20	2.067	20	2.072	10	2.076	10	2.202				
3	1.731							20	2.074	10	2.071
		40	1.694	7	1.697	10	2.056				
5	1.612					3	1.860	7	1.853		
		90	1.601	80	1.600	15	1.838				
20	1.495					30	1.691	5	1.700	5	1.694
100	1.490							50	1.600	30	1.598
		100	1.473	100	1.472			3	1.576		
20	1.465							3	1.500		
						40	1.487				
								100	1.471	100	1.471
						40	1.454				
										3	1.402
Set 7.3		12 hrs @ 800° C.				Set 7.4		12 hrs @ 600° C.			

The zinc ferrite controls show a strong correlation with the ASTM file for this mineral in all samples at all temperatures. In this respect they are quite similar to the nickel ferrite samples, even to the absence of hematite in the lower temperatures. In the last set, 8.4, however, there are two lines which correspond to ASTM lines for metallic zinc. The presence of these lines and the absence of any hematite lines is puzzling, but might be explained by an excess of zinc somehow getting into this particular sample, or by not heating the sample high enough to allow all of the zinc to combine with the iron present.

The Cu,Zn sample in Set 8.1 has good correlation with both of the binary controls, but has lines which can be attributed to cuprite also. Similar lines are found in Set 8.2 but in Set 8.3 they change to those of tenorite as expected. These lines are also found in Set 8.4 along with the zinc lines found in the zinc ferrite control, but no hematite lines. On the above evidence, one can conclude that zinc ferrite is formed in preference to that of copper at all experimental temperatures.

TABLE 8.--Data from the ternary sample Cu,Zn,Fe compared with the binary samples Cu,Fe and Zn,Fe. ^{1}indicates metallic zinc, ^{2}cuprite, ^{3}tenorite.

Cu,Fe		Cu,Zn,Fe		Zn,Fe		Cu,Fe		Cu,Zn,Fe		Zn,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
5	4.833					5	4.762				
		3	4.813					10	2.955	20	2.960
20	2.962	50	2.967			20	2.942				
				7	2.953	100	2.515	100	2.529	100	2.526
		5	2.802					5	2.454		
100	2.527	100	2.537	80	2.526	3	2.411			5	2.421
		5	2.466^2					10	2.099^2	10	2.101
3	2.424	5	2.423	2	2.435	20	2.085				
20	2.097	30	2.102^2	5	2.098	10	1.708	20	1.715	10	1.720
		3	1.915							80	1.622
10	1.716	20	1.722	10	1.717	80	1.611	100	1.609		
60	1.616	80	1.625	80	1.619	90	1.481	100	1.480	90	1.491
60	1.486	80	1.492^2	100	1.488	5	1.416				
		3	1.481								
Set 8.1		16 hrs @ 1000° C.				Set 8.2		12 hrs @ 1000° C.			
15	4.762					3	4.807			3	4.818
20	2.958	40	2.964	20	2.958			3	4.782		
20	2.534	100	2.534^3	100	2.527	3	3.659				
100	2.493					3	2.953	20	2.958	20	2.964
		5	2.470					3	2.784		
10	2.410			10	2.421			100	2.530^3	100	2.534
5	2.302	30	2.300^3			100	2.511				
5	2.135									5	2.435
20	2.067							3	2.465^1	5	2.465^1
		5	1.870			3	2.415	5	2.424		
3	1.731					40	2.317	20	2.316^3		
		30	1.720	10	1.719	10	2.202				
10	1.699							20	2.100^1	10	2.106^1
5	1.646					10	2.056				
		80	1.623	80	1.621	3	1.860	10	1.861		
20	1.612					15	1.838				
20	1.595							20	1.719	10	1.720
100	1.490	80	1.492	90	1.489	30	1.691	80	1.623	80	1.622
20	1.465							10	1.583		
								3	1.512		
						40	1.487	85	1.492	90	1.492
Set 8.3		12 hrs @ 800° C.				Set 8.4		12 hrs @ 600° C.			

Since both the binary controls have been discussed above, this interpretation will be confined to the ternary compounds. With the exception of the lines in Set 9.1, there is little correlation with the manganese control samples, and only slightly better matching with the magnesium ferrite samples. The Mg,Mn lines correlate rather well with the ASTM lines for magnetite and those of magnesioferrite. In Set 9.4, there are some hematite lines, but no evidence for the missing elements. A possible answer for this problem is found in the diadochy of manganese and iron. If this is occurring here, then two products with similar lines could be formed.

TABLE 9.--Data from the ternary sample Mg, Mn, Fe compared with the binary samples Mg, Fe and Mn, Fe. ^{1}indicates hematite.

Mg,Fe		Mg,Mn,Fe		Mn,Fe	
I	d	I	d	I	d
		5	4.993		
		20	2.966	10	2.972
40	2.933				
		100	2.531	100	2.538
100	2.510				
		20	2.103	30	2.109
40	2.084				
		10	1.719	20	1.727
30	1.708				
80	1.611	80	1.621	100	1.627
90	1.480	90	1.490	100	1.497

Set 9.1 16 hrs @ 1000° C.

Mg,Fe		Mg,Mn,Fe		Mn,Fe	
I	d	I	d	I	d
		7	4.838		
				20	3.824
				20	3.656
		20	2.975		
60	2.949				
				100	2.703
		100	2.535		
100	2.518			30	2.509
				30	2.347
				20	2.205
		40	2.107		
5	2.092				
				30	2.004
				60	1.842
20	2.710	20	1.723		
				40	1.693
				80	1.664
80	1.614	80	1.624		
				5	1.526
90	1.483	85	1.490	5	1.488
				10	1.453
				60	1.424

Set 9.1 12 hrs @ 1000° C.

Mg,Fe		Mg,Mn,Fe		Mn,Fe	
I	d	I	d	I	d
5	4.807	5	4.813		
				7	3.
				10	3.633
30	2.951	40	2.955		
3	2.683				
				100	2.647
100	2.519	100	2.526		
				10	2.500
3	2.421				
				10	2.340
				10	2.201
30	2.093	40	2.098		
				10	1.999
3	1.891				
				20	1.839
3	1.891				
20	1.712	20	1.719	5	1.715
3	1.682			10	1.689
				80	1.659
50	1.613	80	1.619		
				7	1.525
100	1.484	95	1.489	20	1.486
3	1.454			50	1.453

Set 9.3 12 hrs @ 800° C.

Mg,Fe		Mg,Mn,Fe		Mn,Fe	
I	d	I	d	I	d
3	4.732				
				3	3.783
		5	3.628^1	10	3.633
3	3.599				
		20	2.951		
20	2.936				
5	2.680	10	2.680^1	100	2.689
		100	2.521^1		
100	2.505			50	2.498
				3	2.335
3	2.271				
		5	2.194^1	20	2.195
30	2.086	25	2.092		
				3	1.999
5	1.835	5	1.833	50	1.835
10	1.708	10	1.714		
5	1.690	10	1.689^1	50	1.690
				40	1.659
30	1.609	50	1.615		
				3	1.597
				3	1.522
100	1.480	100	1.486^1	40	1.485
5	1.452	7	1.452	50	1.452

Set 9.4 12 hrs @ 600° C.

The products of the ternary sample in Set 10.1 are magnesium ferrite and nickel oxide. The correlation between the magnesium ferrite control and that of the ternary sample is apparent. This correlation is also found in Set 10.2 but in the subsequent sets, 10.3 and 10.4, the situation changes slightly, and the correlation is closer with the nickel ferrite control. The line 2.081 is within .03 Angstroms of the strong line of magnesium oxide and 1.478 is within .012 of the second strongest line of magnesium oxide. The high intensity of the 2.081 line could support this position as could the hematite in Set 10.4. On this rather tenuous evidence, it is concluded that at high temperatures, i.e. above 1000° C., magnesium is more easily accepted into the ferrite lattice, but at temperatures below this, the stable form is nickel ferrite.

TABLE 10.--Data from the ternary sample Mg,Ni,Fe compared with the binary samples Mg,Fe and Ni,Fe. [1]indicates N,O.

MgFe$_2$O$_4$		Mg,Ni		NiFe$_2$O$_4$		MgFe$_2$O$_4$		Mg,Ni		NiFe$_2$O$_4$	
I	d	I	d	I	d	I	d	I	d	I	d
		5	4.802							5	4.797
40	2.933	40	2.944					5	4.781		
				5	2.891					30	2.966
100	2.510	100	2.515			60	2.949	10	2.942		
				60	2.491	100	2.518	100	2.507	100	2.506
		10	2.415[1]					10	2.409[1]	5	2.398
40	2.084	70	2.093[1]			50	2.092	70	2.088[1]		
				10	2.072					30	2.079
		5	2.020							3	1.997
30	1.708	10	1.706	10	1.697	20	1.710	10	1.705	10	1.700
80	1.611	70	1.609			80	1.614	70	1.607	70	1.603
				60	1.601	90	1.483	100	1.478[1]	80	1.474
90	1.480	90	1.480[1]	100	1.472					5	1.408
Set	10.1	16 hrs @ 1000° C.				Set	10.2	12 hrs @ 1000° C.			
5	4.807					3	4.732				
30	2.951					3	3.599				
		5	2.929	5	2.918	20	2.936				
3	2.770							10	2.920	5	2.927
3	2.683					5	2.680				
100	2.519					100	2.505				
		90	2.505	90	2.493			100	2.494	40	2.492
3	2.421	5	2.410[1]					10	2.404	3	2.396
				5	2.394	3	2.271				
30	2.093					30	2.086	80	2.079[1]	10	2.071
		50	2.081[1]	10	2.076	5	1.835				
3	2.891					5	1.708				
20	1.712					5	1.690	5	1.697	5	1.694
		5	1.702	7	1.697	30	1.609				
3	1.682							30	1.600	30	1.598
50	1.613	50	1.605	80	1.600	100	1.480				
100	1.484	100	1.478[1]	100	1.472			90	1.474[1]	100	1.471
3	1.454					5	1.452				
										3	1.402
Set	10.3	12 hrs @ 800° C.				Set	10.4	12 hrs @ 600° C.			

The apparent products of Mg,Zn sample in Set 11.1 are zinc ferrite and magnesium oxide. Similar lines are found in the subequent sets with good correlation between the ternary samples and zinc ferrite maintained throughout. This is somewhat different than the results of the Mg,Ni sets, something which might not be expected in view of similarities between the zinc ferrite and nickel ferrite controls. Zinc must be much more acceptable to all temperatures to the ferrite lattice than nickel.

TABLE 11.--Data of the ternary sample Mg,Zn,Fe compared with the binary samples Mg,Fe and Zn,Fe. [1]indicates MgO.

Mg,Fe		Mg,Zn,Fe		Zn,Fe		Mg,Fe		Mg,Zn,Fe		Zn,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
		5	2.958	7	2.953	60	2.949	30	2.955	20	2.960
40	2.933							100	2.527	100	2.526
		80	2.523	80	2.526	100	2.518				
100	2.510									5	2.421
				2	2.435	50	2.092	30	2.07[1]	10	2.101
		20	2.099[1]	5	2.098	20	1.710	30	1.718	10	1.720
40	2.084									80	1.622
		10	1.719	10	1.717	80	1.614	80	1.612		
30	1.708					90	1.483	90	1.488[1]	90	1.491
		80	1.621	80	1.619						
80	1.611										
		5	1.500								
90	1.480	100	1.489[1]	100	1.488						
Set 11.1		16 hrs @ 1000° C.				Set 11.2		12 hrs @ 1000° C.			
5	4.807									3	4.818
30	2.951	40	2.953	20	2.958			5	4.792		
		50	2.799			3	4.732				
3	2.772					3	3.599				
3	2.683							50	2.958	20	2.964
		100	2.527	100	2.527	20	2.936				
100	2.519							10	2.790		
		5	2.470			5	2.680				
3	2.421	5	2.428	10	2.420			100	2.523	100	2.534
30	2.093	40	2.101[1]			100	2.505				
3	1.891							10	2.461		
20	1.712	20	1.718	10	1.719					5	2.435
3	1.682					3	2.271				
		80	1.621	80	1.621			40	2.102[1]	10	2.106
50	1.613					30	2.086				
100	1.484	90	1.489[1]	90	1.489			5	1.905		
3	1.454					5	1.835				
								5	1.785		
						5	1.708	10	1.715	10	1.720
						5	1.690				
						30	1.609	80	1.617	80	1.622
								10	1.497[1]		
						100	1.480	95	1.487	90	1.492
						5	1.452				
Set 11.3		12 hrs @ 800° C.				Set 11.4		12 hrs @ 600° C.			

The Mn,Ni products are apparently maghemite and nickel oxide in Set 12.1. The d-spacings are somewhat low for magnetite but match ASTM lines for maghemite with the exception of 2.406 which can be found in the recorded lines for nickel oxide. In Set 12.2 however there is good correlation between the ternary sample and the nickel ferrite control. Again, there is no sign of manganese and it must be assumed that it is either substituting for iron in some way or is present in an amorphous form as spectrochemical analysis indicates that it is present.

In Set 12.3, there is a good match with the ASTM file and experimental data for nickel ferrite with a possibility of gamma manganese dioxide. The increased intensity of the line 2.090 might be attributed to the latter substance. This is extremely tenuous as the other intense lines for this product are not evident.

Set 12.4 also shows an increased intensity for a line in this area, which might be considered support for the hypothesis. In addition, a strong line of hematite is found.

TABLE 12.--Data of the ternary sample Mn, N, Fe compared with the binary samples Mn, Fe, and Ni, Fe. ^{1}indicates NiO, ^{2}indicates hemetite, and ^{3}indicates gamme MnO_2.

Mn,Fe		Mn,Ni,Fe		Ni,Fe		Mn,Fe		Mn,Ni,Fe		Ni,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
		3	4.767							5	4.797
10	2.972					20	3.824				
		15	2.927			20	3.656				
				5	2.891					30	2.966
100	2.538							10	2.925		
		100	2.510			100	2.703				
				60	2.491	30	2.509	80	2.505	100	2.506
		5	2.406^{1}							5	2.398
30	2.109					30	2.347				
		20	2.090^{1}			20	2.205				
				10	2.072			20	2.085	30	2.079
20	1.727					30	2.005				
		10	1.708	10	1.697					3	1.997
100	1.627					60	1.842				
		70	1.611	60	1.601			20	1.706	10	1.700
100	1.497					40	1.693				
		80	1.481^{1}			80	1.664				
				100	1.472			80	1.610	10	1.603
		3	1.416			5	1.526				
						5	1.488	100	1.481	80	1.474
						10	1.453				
						60	1.424				
								5	1.415	5	1.408
Set 12.1		16 hrs @ 1000° C.				Set 12.2		12 hrs @ 1000° C.			
		10	4.747					7	4.777		
7	3.					3	3.783				
10	3.633					10	3.633				
		30	2.936					15	2.944		
				5	2.918					5	2.927
100	2.697					100	2.689	3	2.691^{2}		
		100	2.515					100	2.515		
10	2.500			90	2.493	50	2.498			40	2.492
		10	2.404^{3}					10	2.410^{3}		
				5	2.394					3	2.396
10	2.340					3	2.335				
10	2.201					20	2.195				
		50	2.090^{3}					40	2.086^{3}		
				10	2.076					10	2.071
10	1.999					3	1.999				
20	1.839					50	1.835				
5	1.715							20	1.708		
		20	1.707			50	1.690			5	1.694
10	1.689			7	1.697	40	1.659				
		80	1.610	80	1.600			80	1.612		
7	1.525					3	1.597			30	1.598
20	1.486	90	1.480	100	1.472	3	1.522				
50	1.453					40	1.485	100	1.480	100	1.471
						50	1.452				
								3	1.418		
										3	1.402
Set 12.3		12 hrs @ 800° C.				Set 12.4		12 hrs @ 600° C.			

Although the d-spacings in sets 13.1, 13.2, and 13.3 correlate well with those of zinc ferrite, they also correlate with lines recorded for magnetite, and manganese iron zinc oxide. For this reason, little can be concluded concerning the order of acceptance of zinc and manganese. In Set 13.4, one also finds lines of hematite amongst those of "zinc ferrite." This does not allow any conclusion to be drawn concerning the question at hand however.

TABLE 13.--Data of ternary sample Mn,Zn,Fe compared with the binary samples Mn,Fe, and Zn,Fe. ^{1}indicates hematite lines.

Mn,Fe		Mn,Zn,Fe		Zn,Fe	
I	d	I	d	I	d
210	2.972				
		10	2.960	7	2.953
100	2.538	100	2.531	80	2.536
		5	2.429	2	2.435
30	2.109	10	2.103	5	2.098
20	1.721	10	1.721	10	1.717
100	1.627	80	1.624	80	1.619
100	1.497	90	1.493	100	1.488

Set 13.1 16 hrs @ 1000° C.

Mn,Fe		Mn,Zn,Fe		Zn,Fe	
I	d	I	d	I	d
20	3.824				
20	3.656				
		20	2.975		
				20	2.960
100	2.703				
		100	2.539		
				100	2.526
30	2.509				
		5	2.441		
				5	2.421
30	2.347				
20	2.205				
		10	2.113	10	2.101
30	2.004				
60	1.842				
		10	1.726	10	1.720
40	1.693				
80	1.664				
		70	1.627	80	1.622
5	1.526				
5	1.488	80	1.495	90	1.491
10	1.453				
60	1.424				

Set 13.2 12 hrs @ 1000° C.

Mn,Fe		Mn,Zn,Fe		Zn,Fe	
I	d	I	d	I	d
7	3.8				
10	3.633				
		20	2.968	20	2.958
100	2.697				
		100	2.530	100	2.527
10	2.500				
		5	2.430	10	2.420
10	2.340				
10	2.201				
		10	2.110		
10	1.999				
20	1.839				
5	1.715	10	1.724	10	1.719
10	1.689				
80	1.659				
		70	1.627	80	1.621
7	1.525				
20	1.486	90	1.494	90	1.489
50	1.453				

Set 13.3 12 hrs @ 800° C.

Mn,Fe		Mn,Zn,Fe		Zn,Fe	
I	d	I	d	I	d
		5	4.828	3	4.818
3	3.783				
		5	3.659		
10	3.633				
		75	2.962	20	2.964
		3	2.795		
100	2.689				
		25	2.679^1		
		100	2.531	100	2.534
3	2.335				
20	2.195	5	2.195		
3	1.999	25	2.104	10	2.106
3	1.999				
50	1.835	10	1.839		
		25	1.721	10	1.720
50	1.690	15	1.691^1		
3	1.659				
		75	1.623	80	1.622
3	1.597				
3	1.522				
40	1.485	75	1.489	90	1.492
50	1.452				

Set 13.4 12 hrs @ 600° C.

The Ni,Zn products are zinc ferrite and nickel oxide in Set 14.1. The match between the ASTM files and nickel oxide is not without question, but the observation that the ternary samples are closer to the zinc ferrite control lends credence to the above conclusions. These products are found in all subsequent sets and are unaccompanied by hematite in Set 14.4. This is to be expected since neither of the control samples were found to have hematite,

TABLE 14.--Data of the ternary sample Ni,Zn,Fe compared with the binary samples Ni,Fe and Zn,Fe. ^{1}indicates NiO, ^{2}indicates metallite zinc.

Ni,Fe		Ni,Zn,Fe		Zn,Fe		Ni,Fe		Ni,Zn,Fe		Zn,Fe	
I	d	I	d	I	d	I	d	I	d	I	d
				7	2.953	5	4.797	5	4.797		
		20	2.936			30	2.966				
5	2.891							20	2.951	20	2.960
				80	2.526			100	2.522	100	2.526
		100	2.513			100	2.506				
60	2.491							20	2.434^1		
		20	2.428^1	2	2.435					5	2.421
		70	2.108	5	2.098	5	2.398				
		20	2.089^1					40	2.110		
10	2.072							30	2.094^1	10	2.101
		70	1.709	10	1.717	30	2.079				
10	1.691					3	1.997				
		80	1.615	80	1.619			10	1.714	10	1.720
60	1.601					10	1.700				
		90	1.494	100	1.488			75	1.617	80	1.622
100	1.472	100	1.484^1			70	1.603				
								50	1.497	90	1.491
						80	1.474	80	1.484^1		
						5	1.408				
Set 14.1		16 hrs @ 1000° C.				Set 14.2		12 hrs @ 1000° C.			
				20	2.958					3	4.818
		10	2.938					2	4.650		
5	2.918							20	2.968	20	2.964
				100	2.527	5	2.927				
		90	2.513					2	2.854		
90	2.493							100	2.526	100	2.534
		5	2.413	10	2.420	40	2.492				
5	2.394							5	2.421	5	2.435
		70	2.090^2			3	2.396				
10	2.076							30	2.096^2	10	2.106
7	1.697	10	1.709	10	1.719	10	2.071				
80	1.600	80	1.612	80	1.621			5	1.714	10	1.720
100	1.472	100	1.482^2	90	1.489	5	1.694				
								30	1.615	80	1.622
						30	1.598				
						100	1.471	90	1.483	80	1.492
Set 14.3		12 hrs @ 800° C.				Set 14.4		12 hrs @ 600° C.			

TABLE 15.--D-spacings and intensities of the three most intense lines of compounds found in this study. After the ASTM Index to the X-ray Powder Data File (1959).

Compound	D-spacings			Intensities		
Copper	2.09	1.81	1.28	100	46	20
Copper iron oxide	2.49	1.49	2.60	100	100	50
Copper oxide	2.52	2.32	2.53	100	96	49
Copper oxide	2.47	2.14	1.51	100	37	27
Alpha iron oxide	2.69	2.51	1.69	100	80	80
Magnetite	2.53	1.48	2.97	100	70	60
Gamma iron oxide	2.52	1.48	2.95	100	53	34
Magnesium	2.45	2.61	2.78	100	41	35
Magnesium ferrite	2.52	1.48	1.61	100	90	70
Magnesium oxide	2.11	1.49	0.94	100	52	17
Manganese ferrite	2.56	2.12	1.64	100	60	60
Bixbyite	2.72	1.66	1.42	100	90	80
Gamma manganese oxide	2.48	2.74	3.08	100	70	60
Hausmannite	2.47	2.74	1.54	100	63	50
Manganese oxide	2.72	1.66	1.42	100	90	60
Manganese iron zinc oxide	2.55	1.49	1.62	100	80	70
Nickel ferrite	2.51	1.48	1.60	100	53	33
Nickel oxide	2.09	2.41	1.48	100	91	57
Zinc	2.09	2.47	2.31	100	53	40
Zinc ferrite	2.53	1.49	1.62	100	80	70
Zinc oxide	2.48	2.82	2.60	100	71	56

DUSCUSSION OF DATA

The general order of acceptance into the ferrite structure seems to be

Zn, Mg, Ni, Cu, Mn,

especially at temperatures of 1000° C. At lower temperatures, Nickel and magnesium change places as discussed above. This sequence is somewhat different than that predicted on the basis of ionic radii and significantly different from that predicted according to Ahrens' theory.

Looking at Table 4, it is observed that both zinc and magnesium have full orbitals, while the remaining four elements have but partially filled d-orbitals. Notice also that nickel is the next element below zinc to have a full s-orbiatal. Thus it appears that electron configuration is the controlling factor in the acceptance of these elements.

These results generally disprove Ringwood's theory (1955) as zinc has a somewhat larger electronegativity than that of magnesium and has a somewhat larger ionic radius than the other ions. This latter quantity is not too significant as all the radii of the ions under examination lie within 15 percent of the radius of zinc, thereby conforming to the Goldschmidt rule. One possible answer for zinc's preference is that the normal configuration of the bonds about the ion is a tetrahedron which might allow the formation of a ferrite lattice with less difficulty than shifting an iron ion into the tetrahedral position.

The samples containing manganese are somewhat of an anomally since they did not form the expected ferrite products. This can perhaps be answered by noting that manganese can substitute readily for any of the other elements due to the variable valence. Palache _et al_. (1944) have several analyses which show that manganese is commonly present with other elements in a ferrite. Mason (1947) found that at 1100° C., a cubic product was obtained with equal amounts of iron and manganese, while at 1000° C., a similar product with a somewhat smaller lattice dimension was obtained with iron, manganese, and zinc in a ratio of about 2.5-2.5-1.0. With this in mind, there seems little doubt that with a ratio of 2-1-1, similar substitutions could occur.

The formation of ferrites in these experiments shows that minerals can be formed at temperatures well below melting points recorded for the mineral. One must be careful however not to forget that these are closed systems and that geologic processes are open systems. Zinc, nickel and iron form common sulfides as does copper, and one should not conclude that ferrites will be formed in preference to sulfides from the data presented above. Temperatures and pressures found in the earth will no doubt effect the conclusions stated above.

CONCLUSIONS

1. Ferrites can be formed at normal pressures and at temperatures of 1000° C. to as low as 600° C. in an oxidizing atmosphere.

2. The substitution of the ferrites will be in the following order:

   magnesium
   Zinc, m~~angane~~se, nickel, copper, manganese.

3. The prime factor controlling this order seems to be the electron configuration of the elements.

SUGGESTIONS FOR FUTURE WORK

More work should be done with the manganese spinels, since they were the most enigmatic of those studied. It is suggested that accurate quantities be combined and the point at which two difinite products are first formed located. This would be most easily accomplished using a ternary system so that quantity versus crystal form could be plotted (see Mason, 1947).

It is also suggested that cadmium and mercury be used in experiements of this type since they are the next elements with full d-shells. Observation of acceptability into the lattice with respect to zinc and mangensium.

Another approach might be to heat the samples under a non-oxidizing atmosphere and/or under pressures of more than one atmosphere to observe any change in the acceptability table found above.

Magnetic susceptability should be measured to observe variation with composition.

In any future work it is suggested that the hydroxides be synthesized by using chlorides of the desired elements rather than sulfates as the reaction

$$ACl_2 + 2NaOH \longrightarrow A(OH)_2 + 2NaCl$$

gives a water soluble and easily removed by-product rather than the sometimes difficult sulfate.

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APPENDIX I

Program to calculate d-spacings of minerals from their powder x-ray films. Adapted from Azaroff and Buerger.

```
         PROGRAM INDEX
      10 READ 11,X2,X1,NUM,LINE,I
      11 FORMAT (2F10.0,A5,215)
         A = X2 + X1
         S = (X2 - X1) * 10,
         B = (S/4,) * .01745
         D = .96865 / SINF (B)
         Q = 1./(D*D)
         PRINT 12, NUM,LINE,I,X2,X1,A,S,D,Q
      12 FORMAT (A7, 217, 6E15.8)
         GO TO 10
         END
         END

         DATA
```

A is a check on the accuracy of measurement of the lines. If done correctly, the column in the print out should not differ except in the third decimal place. S gives the arc length, B the angle of refraction, D the d-spacing.