

## 32. ELECTRON MICROPROBE ANALYSES OF SOME TITANOMAGNETITE GRAINS FROM HOLE 395A<sup>1</sup>

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### INTRODUCTION

The mineral responsible for the magnetic properties of almost all submarine basalts is a member of the magnetite-ulvospinel solid solution series and its oxidized equivalents. These opaque phases have been studied intensively in recent years in an attempt to test the reliability of paleomagnetic results. Although magnetic tests can be performed on samples of any grain size, the extremely small size of the opaque minerals in submarine pillow basalts has limited their study to the reflected light microscope and electron microprobe. The recovery during Leg 34 of coarse-grained massive flow material from the Nazca plate allowed the first attempt at detailed analyses of the titanomagnetite grains. A compilation of the very limited number of microprobe analyses to date (Johnson and Hall, in press) indicates that the magnetic mineral in the Nazca plate massive flows is  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ , where  $x = 0.62 \pm 0.04$ . This value agrees closely with the value of  $x = 0.64$  obtained by Petersen (1976) for subaerially erupted tholeiitic basalts. The recovery from Hole 395A of some coarse-grained basalt extrusives and dikes at various levels within the drill core provided the opportunity to look at the composition of the magnetic minerals in submarine basalts from a slow-spreading ridge from a different ocean and of a different age. The presence of three magnetic reversals within the drill core allows us to examine the magnetic minerals and how their composition varies during the formation of a vertical cross-section of oceanic crust. The wide range of low-temperature alteration within the core also allows us to determine if the magnetic minerals change systematically in composition with progressive low-temperature oxidation.

### EXPERIMENTAL METHOD

The equipment used during this study was an ARL-SEM-Q electron microprobe equipped with nine spectrometers and located at the Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. Analyses were corrected for drift, X-ray absorption, and for secondary X-ray fluorescence. Ten samples from Hole 395A and one from Hole 319A (Leg 34)

were prepared as polished thin sections. Three of the samples are from the dolerite intrusions, which are from Cores 61 to 64 in Hole 395A. The remainder of the Hole 395A samples are from probable extrusive units. The sample from Hole 319A (Leg 34) is from a massive flow unit in the Nazca plate. All titanomagnetite grains were analyzed for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ , and  $\text{Cr}_2\text{O}_3$ . In all cases,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ , and  $\text{Cr}_2\text{O}_3$  were at concentrations too low to be reliably determined, and are not reported here. The remainder of the cation concentrations, as well as the Curie temperatures of the samples, are shown in Table 1. The computer program associated with the microprobe calculates all detectable iron as  $\text{FeO}$ , and since this is not true for titanomagnetites or their oxidized equivalents, the totals obtained by summing all the detectable oxide concentrations will be somewhat less than 100 per cent. The unoxidized, titanium-free magnetite used as a standard gave a total of approximately 90.9 per cent. Adding titanium to the solid solution  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$  increases the number of ferrous ions at the expense of the ferric ions, and the totals for the unoxidized samples in this study should be somewhat higher than the magnetite standard.

In general, five spot analyses were done on each titanomagnetite grain and five grains, chosen at random, were done on each sample. Thus the data in Table 1 represent the average of approximately 25 analyses of nine elements for each sample. The only exceptions to this were the two fine-grained pillow basalts (Samples 395A-27-2, 145-147 cm and 395A-48-1, 55-57 cm) where fewer than five grains were analyzed for each sample. Since the electron beam was 1 to 3 microns in size it was difficult to find grains in these two samples that were large enough to analyze. Attempting analyses in grains smaller than about 5 microns caused beam spreading into the surrounding (and underlying) silicate phases. This beam spreading was immediately detectable as a dramatic rise in  $\text{SiO}_2$  content, and these analyses are not included in the sample averages.

Five spot analyses were done on each of two standard samples (ilmenite USNM 96189 and magnetite USNM 114887) before and after each sample measurement. All data were corrected for any machine drift by normalization of the standard analyses. A 10-sec counting time was used, and the data were subjected to Bence-Albee corrections within the microprobe computer program.

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TABLE 1  
Electron Microprobe Analyses of Opaque Minerals, Hole 395A

| Sample<br>(Interval<br>in cm)                   | Al <sub>2</sub> O <sub>3</sub> | FeO   | MgO  | MnO  | TiO <sub>2</sub> | Total | Fe <sub>3-x</sub> Ti <sub>x</sub> O <sub>4</sub><br>(x100) | FeO/TiO <sub>2</sub> | Curie<br>Temp.<br>(°C) | Comments   |
|---|--------------------------------|-------|------|------|------------------|-------|--|----------------------|------------------------|--|
| 395A-5-1,<br>89-91                              | 1.59                           | 70.44 | 1.31 | 0.62 | 21.08            | 95.03 | 58.81  | 3.34                 | 122                    | Aphyric basalt   |
| 395A-5-2,<br>6-8                                | 1.22                           | 70.86 | 1.06 | 0.65 | 21.10            | 94.90 | 58.87  | 3.36                 | 145                    | Same unit as 5-1   |
| 395A-15-1,<br>76-78                             | 1.57                           | 69.73 | 1.05 | 0.57 | 20.62            | 93.55 | 57.53  | 3.38                 | 197                    | Plagioclase-olivine<br>phyric basalt                             |
| 395A-15-2,<br>55-57                             | 1.35                           | 70.80 | 0.79 | 0.61 | 20.91            | 94.45 | 58.34  | 3.39                 | 195                    | Same unit as 15-1  |
| 395A-16-1,<br>63-65                             | 1.09                           | 67.87 | 0.51 | 0.60 | 21.57            | 91.64 | 60.18  | 3.15                 | 256                    | Plagioclase-olivine<br>phyric basalt                             |
| 395A-27-2,<br>145-147<br>(3 grains<br>analyzed) | 1.41                           | 64.21 | 0.52 | 0.70 | 22.73            | 89.58 | 63.42  | 2.82                 | 211                    | Plagioclase-olivine-<br>CPX phyric basalt<br>fine-grained pillow |
| 395A-48-1,<br>55-57<br>(2 grains<br>analyzed)   | 1.77                           | 68.10 | 0.98 | 0.77 | 19.30            | 90.48 | 53.85  | 3.52                 | 202                    | Aphyric basalt, fine-<br>grained pillow                          |
| 395A-61, CC,<br>13-15                           | 1.28                           | 67.88 | 0.51 | 0.64 | 22.53            | 92.84 | 62.86  | 3.01                 | 274                    | Upper dolerite<br>intrusion                                      |
| 395A-63-2,<br>2-4                               | 1.16                           | 66.33 | 0.80 | 0.79 | 24.44            | 93.53 | 68.19  | 2.71                 | 180                    | Lower dolerite<br>intrusion                                      |
| 395A-64-1,<br>106-108                           | 0.82                           | 71.43 | 0.39 | 0.62 | 21.82            | 95.08 | 60.88  | 3.27                 | 121                    | Lower dolerite<br>intrusion                                      |
| 319A-3-2,<br>108-111                            | 1.49                           | 63.87 | 0.48 | 0.79 | 24.46            | 91.09 | 68.24  | 2.61                 | 336                    | Leg 34 sample from<br>the Nazca plate                            |

## RESULTS

The first five samples (Table 1; Samples 395A-5-1, 89-91 cm, through 395A-16-1, 63-65 cm) are from several different extrusive basalt units in the uppermost normal magnetic polarity unit (Johnson, Paleomagnetic results from igneous rock samples, this volume.) Samples 395A-27-2, 145-147 cm and 395A-48-1, 55-57 cm are from two different rock types within the middle reversely magnetized polarity unit. Sample 395A-61, CC, 13-15 cm is from the upper dolerite intrusion, and Samples 395A-62-2, 2-4 cm and 395A-64-1, 106-108 cm are from the lower (and probably contemporaneous with the upper) dolerite intrusion. The last sample, 319A-3-2, 108-111 cm, is a sample of a massive flow unit from the Nazca plate. The Nazca plate sample was included in this study because none of the coarse-grained Leg 45 samples were sufficiently oxidized to have Curie temperatures exceeding 300°C. This addition of a highly oxidized sample from another DSDP leg (indeed, from another ocean) may introduce some bias into the following discussion. However, we feel it is important to include the widest possible range of low-temperature oxidation states in order to aid in the interpretation of our results.

Table 1 shows the Curie temperatures for the samples used in this study. These were determined by heating (approximately 50°C/min) in a Curie balance, in an atmosphere of 9 percent hydrogen and 91

percent nitrogen (Johnson, Rock magnetic properties of igneous rock samples, this volume.) Since titanomagnetites from submarine basalts drilled during previous DSDP legs have been found to be of relatively uniform initial composition, the elevation of Curie temperature from an initial 120°C to 400°C is a fairly reliable guide to the extent of low-temperature oxidation (Johnson and Hall, in press).

The composition of the titanomagnetite grains, in terms of Fe<sub>3-x</sub>Ti<sub>x</sub>O<sub>4</sub>, is also shown in Table 1. It should be noted that the use of *x* in the relationship Fe<sub>3-x</sub>Ti<sub>x</sub>O<sub>4</sub> has, in the past, implied that oxidation is a "constant cation" process. Since we will argue later that this is not the case, the definition of *x* for oxidized phases will have to be modified slightly. The "average" value of *x* can be determined several ways: by grouping the same rock units together, by grouping the unoxidized samples together, by grouping the same polarity units together, or by just combining all the sample averages. The table below shows these various averages.

|   | <i>x</i> (x100) in<br>Fe <sub>3-x</sub> Ti <sub>x</sub> O <sub>4</sub> (±1 S.D.) |
|---|--|
| All samples together  | 61.01 ±4.40  |
| All Hole 395A samples together  | 60.29 ±3.89  |
| Combining similar rock units  | 61.54 ±4.76  |
| Only samples with Curie temperatures<br>below 200°C combining<br>similar rock units | 60.44 ±3.58  |

Since, as we will argue later, progressive low-temperature oxidation causes a reduction in the iron content and a decrease in the FeO/TiO<sub>2</sub> ratio in titanomagnetite grains, the last averaging technique is the most likely to be correct for determining the original composition of the magnetic grains. In any case, there is not a wide range of compositions represented in the table above. The average values of  $x = 0.60 \pm 0.04$  are somewhat lower than those of  $x = 0.62 \pm 0.04$  obtained previously from Leg 34 submarine basalts, but are within 1 standard deviation. This difference may occur because the previous samples were more highly oxidized (Curie temperatures were not determined for the same samples as the microprobe analyses during Leg 34), because of a small but systematic difference between the Mid-Atlantic Ridge and the Nazca plate basalts, or because of systematic analytical differences.

Since an increase in Curie temperature above 150°C is a good indicator of the degree of progressive low-temperature oxidation of titanomagnetite to titanomaghemite (Readman and O'Reilly, 1972; Ozima and Sakamoto, 1971; Johnson and Merrill, 1973), sample correlation coefficients were calculated between Curie temperature and the various elemental abundances (%). This was done to see if there were any systematic changes in titanomagnetite composition during progressive low-temperature oxidation. The table below shows the calculated sample correlation coefficients,  $r$ , where  $r$  varies between  $\pm 1$  and  $-1$ . For  $r = 0$ , a linear regression does not explain anything about the variation of one parameter with the other.

$r$  (linear correlation coefficient)

|                                |        |
|--------------------------------|--------|
| Al <sub>2</sub> O <sub>3</sub> | +0.197 |
| MgO                            | -0.526 |
| MnO                            | +0.340 |
| TiO <sub>2</sub>               | -0.554 |
| FeO                            | -0.714 |
| FeO/TiO <sub>2</sub>           | -0.559 |

The 5 per cent and 1 per cent significance levels for these correlations are 0.576 and 0.708, respectively. Figure 1 shows a plot of total iron content (expressed as FeO) as a function of Curie temperature. The large scatter in the data is not completely convincing, but the negative correlation coefficient for FeO in the table above (significant at the 1% level) seems to indicate a reduction of total iron content with progressive low-temperature oxidation. Figure 2 shows the FeO/TiO<sub>2</sub> ratio as a function of Curie temperature. The scatter in these data and the lower correlation coefficient in the table above are less convincing than for total iron, but are consistent with a general decrease in the FeO/TiO<sub>2</sub> ratio with increasing degree of low-temperature oxidation. The correlation coefficients in the above table test for linear relationships. Although there is no reason to believe that the FeO/TiO<sub>2</sub> ratio will decrease linearly with oxidation, this approximation is a valid estimate of the data trend, and the data are insufficient to justify higher order trend analyses.

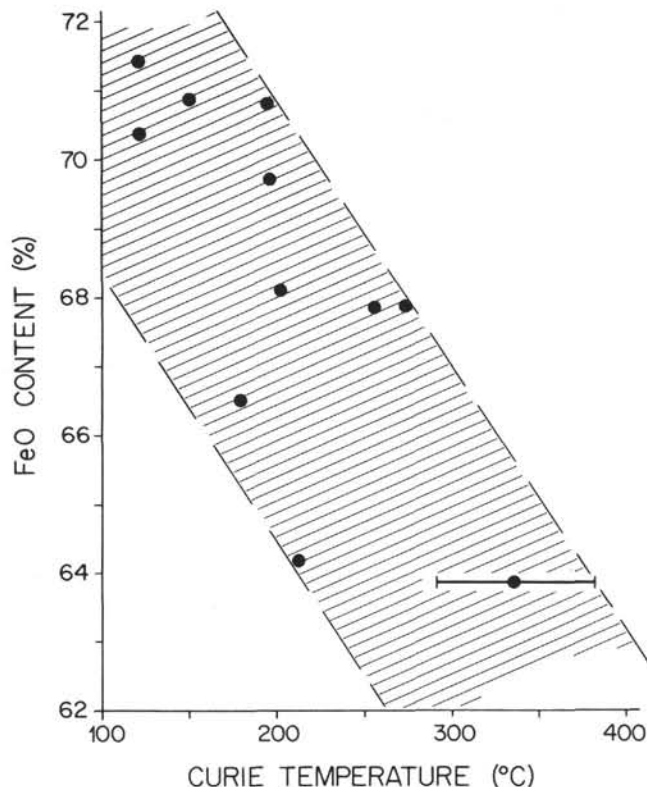


Figure 1. Iron content of the titanomagnetite/titanomaghemite grains as a function of sample Curie temperature. Each solid data point represents 5 analyses each of 5 separate grains from each sample (25 analyses total from each sample). The horizontal bar for the highest Curie temperature sample is to indicate that there were 2 Curie temperatures measured from this sample and that they differed by almost 100°C.

Figure 3 shows the variance (the square of one standard deviation) of the "within-grain" iron content as a function of Curie temperature. Multiple analyses, usually five or six, were made at random locations within each titanomagnetite grain. The variance of these "within-grain" measurements, averaged over 5 grains for each sample, is a measure of how much the total iron content can vary within each titanomagnetite grain. Since it is known that low-temperature oxidation is a non-uniform process, it would be expected that unoxidized samples would show a small variation in iron content and that this variation would increase with increasing oxidation. Figure 3 shows that this is indeed the case. The horizontal line is the average variance obtained by multiple analyses of a single standard Ilmenite grain. If we assume that the ilmenite grain has uniform composition, then no physical significance can be attached to variances that are less than this value. However, the four highly oxidized samples all show significant variance.

Figure 4 shows the plot of the "between-grain" variance in iron content for these samples as a function of Curie temperatures. By the same argument as before, i.e., that low-temperature oxidation is inherently a non-uniform process, it is expected that the

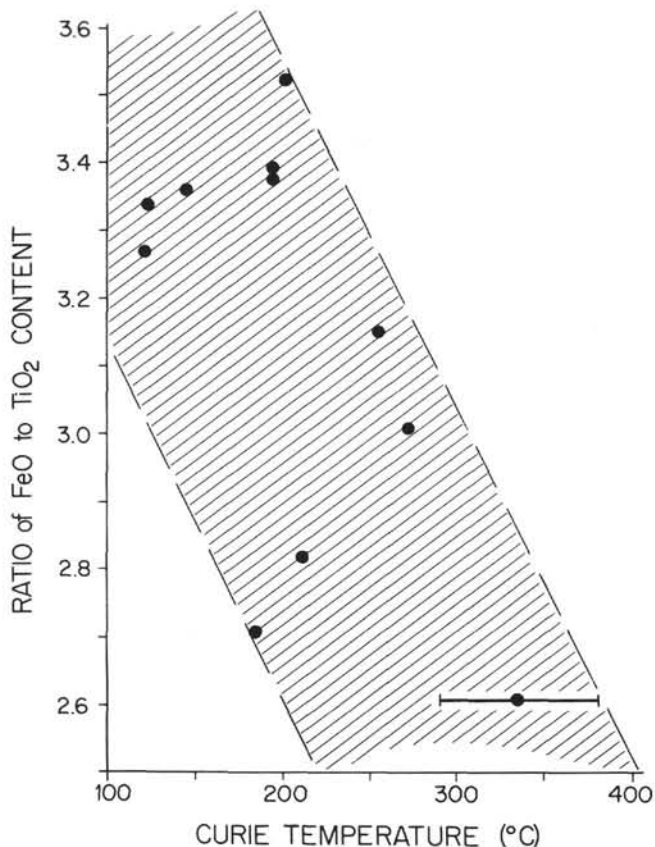


Figure 2.  $FeO/TiO_2$  ratio of the titanomagnetite/titanomaghemite grains as a function of Curie temperature. As pointed out in the text, the total iron content is calculated as FeO, and this does not imply anything about the oxidation state of the iron cations.

“between-grain” variation in composition of the titanomagnetites would increase with oxidation. Figure 4 is consistent with this hypothesis, but the shaded area indicating a functional dependence relies heavily on the high Curie temperature data point (the Leg 34 sample), and so is less convincing.

**DISCUSSION AND CONCLUSIONS**

Examination of Table 1 does not show any readily visible trends in the initial titanomagnetite composition with depth in the hole. The composition ( $x$  values in  $Fe_{3-x}Ti_xO_4$ ) in the dolerite intrusion samples seem slightly higher than most of the extrusive pillows, but this is probably within the range of natural variation. As mentioned previously, the average value of  $x = 0.60 \pm 0.04$  for the unoxidized titanomagnetites from this core is consistent with, but somewhat lower than, the values of previously measured titanomagnetites from submarine basalts. It is also slightly lower than the average value of  $x = 0.064$  obtained by Petersen (1976) for subaerially erupted tholeiitic basalts. An unoxidized grain of titanomagnetite with a composition of  $x = 0.60$  will have a Curie temperature of approximately  $170^\circ C$  (Readman and O’Reilly, 1972; Ozima and Sakamoto, 1971). The addition of several per cent

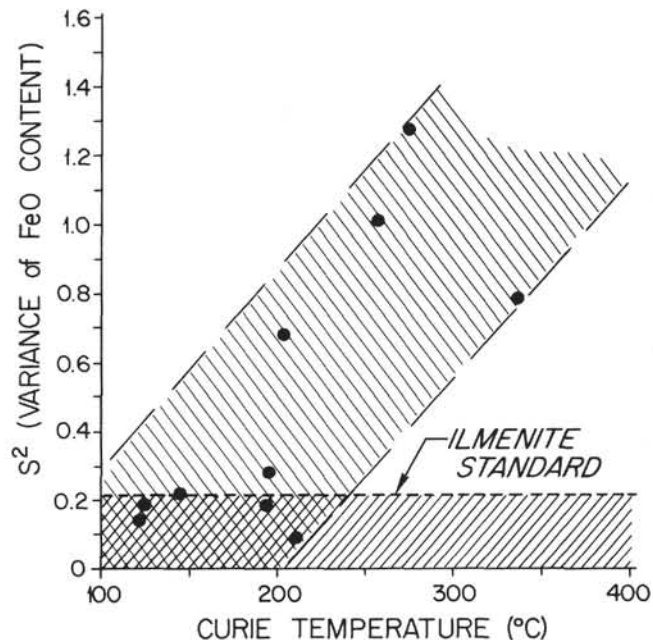


Figure 3. A plot of the “within-grain” variance of the total iron content of the opaque grains as a function of Curie temperature. The horizontal shaded field is the value obtained by repeated measurements of a single ilmenite standard grain.

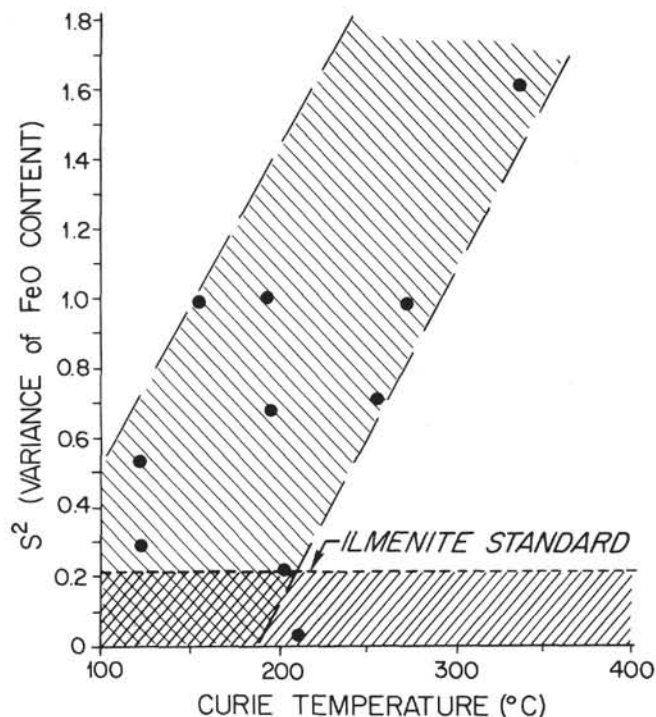


Figure 4. A plot of the “between-grain” variance of the total iron content of the opaque grains as a function of Curie temperature.

total of aluminum, magnesium, and manganese cations to the titanomagnetite lattice would reduce the Curie temperature for the unoxidized magnetic mineral to between  $120^\circ C$  and  $150^\circ C$ . This is consistent with

what has been found in unoxidized submarine basalts from the Mid-Atlantic Ridge (Schaeffer and Schwarz, 1970; Carmichael, 1969; Ryall and Hall, 1976; Johnson and Atwater, 1977), from the Juan de Fuca Ridge (Marshall and Cox, 1972), and from the Nazca Plate (Grommé and Mankinen, 1976; Lowrie and Kent, 1976; Ade-Hall et al., 1976). It is also consistent with the Curie temperatures of the unoxidized titanomagnetites from this (395A) drill core (Johnson, Rock magnetic properties of igneous rock samples, this volume).

The most convincing trend visible in Table 1 is the decrease in total iron content (Figure 1) and the corresponding decrease in the FeO/TiO<sub>2</sub> ratio (Figure 2) with increasing degree of low-temperature oxidation. The correlation coefficients listed above show a general decrease in all cations with oxidation, except aluminum and manganese, and these two variations are not significant. The decrease in iron content with increasing oxidation is significant at the 1 per cent level. This decrease in iron content is consistent with petrological studies of the opaque minerals from submarine and subaerial basalts (Prevôt et al., 1968; Marshall and Cox, 1972; Grommé and Mankinen, 1976; Johnson and Hall, in press). These studies have shown that as the original titanomagnetite grains oxidize at low temperature, a red iron oxide/hydroxide halo forms in the surrounding silicates, and shrinkage cracks appear in the opaque grains and are eventually filled with non-opaque material. In the final stages of low-temperature oxidation, the original titanomagnetite grains are almost completely replaced by non-opaque material, and only a few remnants of highly oxidized titanomaghemite are left to identify the magnetic grain (Johnson and Hall, in press). The data in Figures 1 and 2 and in the list of correlation coefficients, indicating the migration of iron out of the opaque grains and a decrease in the FeO/TiO<sub>2</sub> ratio during oxidation, add credibility to this model. An effort was made during this study to determine the composition of the non-opaque material that was replacing the titanomaghemite, but none of the elements analyzed showed a significant increase in concentration with progressive oxidation.

It should be noted here that the relationship shown in Figures 1 and 2 is strictly related to oxidation. Previous work on synthetic titanomagnetites (Readman and O'Reilly, 1972; Ozima and Sakamoto, 1971) has shown that if the iron content in unoxidized titanomagnetites is *decreased*, the Curie temperature will also *decrease*. This is also true for synthetic titanomaghemites of a given oxidation state. Therefore, the elevation of Curie temperature observed in this study is related to the degree of low-temperature oxidation. The decreasing iron content, which is correlated with the increasing Curie temperature, must be an effect of this oxidation. Previous models for the low-temperature oxidation of titanomagnetite to titanomaghemite have described this as essentially a "constant cation" process. From Figures 1 and 2 it seems clear that, for submarine basalts and Curie temperatures higher than

200°C, this is not the case. It also appears that the variation in composition for individual titanomagnetite grains increases with increasing degree of oxidation.

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