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Key Points:
• Modern oceanographic measurements help define regions for FeMn crust exploration.
• Seawater oxygen is a critical control on the Mn and Co content in FeMn crusts.
• Increased seawater carbonate may influence Fe content in FeMn crusts with water depth.

Supporting Information:
• Supporting Information S1
• Table S1

Correspondence to:
K. Mizell, kmizell@usgs.gov

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Abstract The major controls on the variability of ferromanganese (FeMn) crust composition have been generally described over the past 40 years; however, most compilation studies lack quantitative statistics and are limited to a small region of several seamounts or compare FeMn crusts from disparate areas of the global oceans. This study provides the first detailed research to address the geographic and oceanographic controls of FeMn crust composition from a line of seamounts across 30° of latitude in the west central Pacific. Element concentrations from the uppermost layer (<15 mm) of 57 FeMn crusts were evaluated for statistically significant variance and correlation with a variety of oceanographic and geographic parameters. Manganese, Co, Ni, Mo, and Zn concentrations in crusts in this region are highly anticorrelated with seawater oxygen concentrations, suggesting oxygen as the dominant controlling factor for these elements. Iron instead correlates with water depth, which we attribute to increased carbonate ion concentration with increasing water depth. Silicon, and Al content in crusts demonstrate a potential meridional variance of detrital inputs and sources in the region. Iron, Ba, and Mg are enriched in FeMn crusts below the equatorial upwelling zone which is related to biological productivity. Fluctuations in the four oceanographic and geographic parameters, seawater oxygen content, detrital input, surface productivity, and deep sources of iron, are robustly recorded by FeMn crusts. Modern measurements of these primary parameters, as well as paleoceanographic reconstructions, can be used to define regions of interest for FeMn crust exploration.

1. Introduction
1.1. FeMn Crusts

Ferromanganese (FeMn) crusts are chemical sedimentary rocks composed predominantly of iron and manganese oxide minerals. These deposits grow on the flanks and summits of seamounts and other midplate volcanic edifices throughout the global ocean. They are a hydrogenetic mineral deposit, forming by the precipitation of iron and manganese oxides from seawater and accumulate a remarkable list of elements over time through a variety of sorption reactions. FeMn crust composition is thus dependent on seawater composition, which can vary based on geographic location and water depth, especially with proximity to coastal and eolian input of detritus or to hydrothermal activity, with changes in atmospheric circulation and surface productivity, and as different water masses circulate and mix. The capacity of fluctuations in these oceanographic and geographic controls on seawater composition to be recorded and archived by FeMn crusts must be calibrated, and many studies have done so using isotopes of specific elements like Pb (e.g., Christensen et al., 1997; Klemm et al., 2007), Nd and Hf (van de Flierdt et al., 2004), Os (e.g., Klemm et al., 2005), Ni (e.g., Gall et al., 2013), Ti (e.g., Nielsen et al., 2009), and others. Some studies have also looked at water depth controls on crust composition, for example, variability along a single seamount (Usui et al., 2017) and variability of rare earth elements plus yttrium (REY) with water depth (Azami et al., 2018).

However, few studies have included seawater changes recorded by FeMn crusts along a large, continuous geographic feature where changes with latitude and water depth can covary, and systematic investigations are required to separate the fundamental controls of each variable on crust compositions. Hein et al. (2016) performed one of the few such studies, reporting FeMn crust variability along the 5,000 km long Ninetyeast Ridge
in the Indian Ocean, including changes in growth rates explained by changes in the depth of the oxygen minimum zone (OMZ) and supply of deep-sourced iron; however, that study included only 12 crusts from nine locations along the ridge due to limited sample availability. The research presented here provides another opportunity, but with a much higher sample density, through the examination of 57 FeMn crust samples along a chain of seamounts in the Pacific Ocean that spans from 14°N to 14°S and from 171°W to 168°E (Figure 1). In addition, the current study compares recent growth-layer composition with modern seawater parameters that are easily observed or measurable at the current crust locations, which aids in the development of successful exploration criteria for these deposits by improving the ability to predict FeMn crust composition within large-scale, contemporary, oceanographic, and geographic settings.

1.2. Geographic and Geologic Setting

The Pacific plate hosts several linear volcanic chains composed of a multitude of seamounts as a result of hotspot volcanism and plate movement through time. The central West Pacific Ocean contains the “Hotspot Highway,” a region where four hotspot tracks (Rurutu, Macdonald, Rarotonga, and Samoa) overlap resulting in seamounts of varying composition and ages (Finlayson et al., 2018). FeMn crusts from this study were sampled from a linear chain of seamounts along the Rurutu, Macdonald, and Samoa hotspot tracks, including the Marshall Island, Gilbert Island, Tuvalu, and Tokelau chains, seamounts near Howland and Baker Islands, and the eastern and western Samoan seamounts (Finlayson et al., 2018; Jackson et al., 2010). These seamounts range in age from 10 to 90 million years old and present vast areas of rock outcrops that allow for significant accretion of FeMn crusts (Finlayson et al., 2018).

1.3. Oceanographic Regimes

The FeMn crust sample set spans not only a wide range of latitudes (14°N to 14°S) and longitudes (168°E to 171°W) but also water depths (1,399 to 4,354 m), allowing for the samples to be situated within a variety of water masses (Bostock et al., 2010) and oceanographic environments. The most prominent oceanographic feature in this region is the equatorial upwelling zone (hereafter called EUZ) where upwelled nutrient-rich waters along the equator spur increased biological productivity in surface waters. This results in increased surface chlorophyll-a values occurring along the equator from 3°N to 2.7°S at the western margin of the sample region and from 7°N to 8.8°S at the eastern margin (NASA 2019; Figure 1). Although the EUZ is a feature at the sea surface and FeMn crusts in this study are found below 1,000 m, biogenic particle flux from the surface to deeper levels in the water column is increased under the EUZ (Smith et al., 1997). Scavenged elements like Co, and

Figure 1. Maps of the western equatorial Pacific region studied here including FeMn crust dredge locations. Left: Inset in the upper right shows the general region of the sample area; different colors for dredge locations indicate the four cruises included in this study, and the areas outlined in white show the samples included in each of the three main sample transects, Marshall-Gilbert-Tuvalu (MGT), Samoa, and Howland-Baker-Tokelau (HBT); this map was created in ArcGIS and includes GEBCO 2014 bathymetry. Right: Dredge locations shown on a map of surface chlorophyll-a values (NASA 2019) to show sample locations with respect to increased surface productivity in the equatorial upwelling zone (EUZ).
organic-matter related elements like Ba, can be delivered to deeper parts of the water column when particles are remineralized (Hawco et al., 2018; Paytan & Kastner, 1996). Carbonate particles will also dissolve as they approach the aragonite and calcite compensation depths (ACD and CCD), and biogenic silica particles will dissolve due to its undersaturation everywhere in the oceans. These dissolution processes can return metals to the dissolved phase, making them available for incorporation into adjacent FeMn crusts (Halbach & Puteanus, 1984; Twining & Baines, 2013). In addition, increased carbonate ion concentrations increase pH, which can affect Fe-oxide precipitation (King, 1998).

Beyond productivity-related chemical signals, the water depth at which each FeMn crust was located also determines which of the larger-scale oceanic water masses advected to the region influence each crust. The shallowest and northernmost samples will be influenced by the Eastern Tropical North Pacific subsurface OMZ; for example, two of the FeMn crusts were growing in waters currently containing approximately 90 μmol/L oxygen (Garcia, et al., 2014a). On the other hand, the deepest samples formed in more oxygen-rich circumpolar deep water (~200 μmol/L; Garcia, et al., 2014a; Figure 2). In general, in this region, oxygen concentration increases with water depth, making oxygen a likely control on variation in FeMn crust composition with water depth because of the many redox processes (Hein et al., 1997) that characterize the formation and composition of crusts.

Samples along this meridional transect may also be influenced by multiple detrital inputs. For example, wind-blown loess from Mongolia is known to reach the equatorial north Pacific through the washing out of dust particles from the atmosphere within the intertropical convergence zone (Hyeong et al., 2005), and thus, the northernmost and westernmost FeMn crusts may reflect chemical signatures of this detrital source. Samples in the southeastern region are much closer to the Tonga-Kermadec Volcanic Arc system and may receive more terrestrial/volcanic input, as well as wind-blown loess from Australia as found in nearby deep-ocean sediment cores (Zhou & Kyte, 1992). Another potential influence on crust compositions in the southern part of the study region is hydrothermal activity from the nearby volcanic arcs, back arcs, and hot-spot volcanic activity. In our study, we decipher detrital signatures from bulk FeMn crust compositions to assess this technique, but we acknowledge that isolating the detrital grains and measuring their detailed isotopic (Nd, Pb, and Hf) compositions would better identify these detrital sources.

2. Methods

2.1. Samples

Samples analyzed in this study (n = 57) were collected via dredge on four research cruises (Table 1). Each dredge latitude, longitude, and water depth were calculated from shipboard dredge log records to account for the length of wire out, movement by the ship, approximate seamount slope, and multiple “bites” of the dredge in order to maximize location accuracy. For simplicity in data interpretation, samples were
This study would be best performed with FeMn crust subsamples of only the uppermost 0.5–1 mm of crust in order to minimize the number of years of seawater chemistry that are integrated over each crust sample and for better comparison with modern seawater parameters; however, data from the upper 0.5–1 mm or less were very limited since we compiled previously analyzed samples. In order to maximize the number of samples included in the data set for the best statistics and geographic coverage, we therefore include FeMn crusts and uppermost crust sublayers of up to 15 mm thick. The typical growth rates of FeMn crusts in the open ocean range from 1 to 10 mm/Myr (Hein & Koschinsky, 2014). If a slow growth rate of 1.5 mm/Myr is assumed for samples with the maximum allowed thickness of 15 mm, this would encompass a maximum of 10 Myr of crust growth. Based on models of Pacific Plate movement, a seamount in the study region would have moved ~1° or ~100 km northwest in 10 Myr (Van Hinsbergen et al., 2015). Ten Myr at an average subsidence rate of 2 cm/10^3 yr (Menard, 1969) results in ~200 m of total subsidence. Thus, limiting the thickness to 15 mm still eliminates major variations that might otherwise be attributed to movement of the Pacific plate and associated thermal subsidence, such as movement into or out of the EUZ (latitude) or further below the OMZ (depth). Our data indicate that chemical variations are still interpretable using modern geographic and oceanographic parameters but would be even more robust using thinner crusts to minimize the amount of time integrated within each crust layer. We also acknowledge that some correlations may be stronger if crust layers from a uniform time frame were used.

### 2.2. Major and Trace Element Concentrations

The uppermost layer of each FeMn crust was sampled with a knife and then ground to 75 μm with an agate mortar and pestle. The chemical composition of the Fe-Mn crusts was determined at SGS Labs, Canada (previously XRAL). The 10 major elements were determined by X-ray fluorescence on boron fused disks, and the minor elements by inductively coupled plasma mass spectrometry and atomic emission spectroscopy (ICP-MS and ICP-AES) following a four-acid digestion, except the Tuvalu (cruise RR1310) samples for which Cu, Mo, Ni, V, and Y were prepared for ICP-MS using lithium-metaborate fused disks. The water content (H2O) of each FeMn crust was determined by gravimetric analysis, and the weight percent water was then used to correct element concentrations in each sample to sorbed-water-free values. Reproducibility measured from duplicate analyses of the sample was better than 7% for all elements except for As and Cd, which were 9.3% and 17%, respectively, for one batch out of six separate batches of analyses for which duplicate analyses were measured. Accuracy was determined for four of the seven batches of analyses by calculating the percent difference between published recommended values and measured values for certified reference materials. Accuracy was better than 7% for Fe, Si, Al, Na, K, Ti, P, As, Cd, Cu, and Sr; 8–15% for Pb, Mo, Mg, Mn, Zn, and Ba; 15–25% for Y, Ca, Cr, and Co; 27% for V; and 34% for Ni. Certified reference materials used to determine accuracy included: SY-4, NODA-1, NODP-1, OREAS 171, OREAS 405, OREAS 903, SARM42, and RTS-3A. Note that some certified standards measured for accuracy calculations are dissimilar to FeMn crust matrix and may not closely reflect the accuracy for the FeMn crust measurements presented here. For dredge sites with multiple individual FeMn crust samples, the chemistry from the uppermost layers of these samples was averaged and represents the mean chemical composition of the upper <15 mm of FeMn crusts at the particular latitude, longitude, and depth of the dredge site.

### 2.3. Statistical Correlations and Factor Analysis

To determine statistically significant variance in major and trace element concentrations for FeMn crust samples from different locations along the seamount chains, and to determine correlations for concentration variations with geographic and oceanographic parameters, several statistical methods were employed.
Variance between samples was first determined using basic parameters such as mean and standard deviation. Pearson correlation coefficient matrices (CCM) were generated using MatLab to determine element concentration correlations with geographic and oceanographic parameters that could be quantified, such as latitude, longitude, water depth, and oxygen concentration. Longitudes were all converted to eastings so that longitude increases toward the east. To investigate all geographic factors and identify possible inherent location biases in the data set, CCM were run separately for the whole data set (n = 57), the primary MGT transect (n = 33), HBT transect (n = 9), MGT samples within the latitude bounds of the HBT transect (n = 15), and the Samoa transect (n = 15). Samples north of the equator (n = 12), all samples south of the equator (n = 45), and samples north and south of the equator within the MGT transect (n = 10 and n = 23, respectively) were also run in separate CCM in order to account for the larger overall number of samples south of the equator. Note that all correlations reported in subsequent sections are significant at the 95% confidence level (CL) or higher, with specific CLs (95% or 99%) defined when important. Q-mode factor analysis of the major and trace element data was also run for the primary MGT transect (n = 33) in MatLab (Pisias et al., 2013) to identify common groups of elements, referred to as factors, and determine which of these factors reflect geographic and oceanographic parameters along this primary transect. For Q-mode factor analysis, each variable percentage was scaled to the percent of the maximum value before the values were row-normalized and cosine-theta coefficients calculated. Factors were derived from orthogonal rotations of principal component eigenvectors using the Varimax method (Klovan & Imbrie, 1971). All but three samples have communalities greater than 0.9 with an overall average communality for the 33 samples of 0.94; communality is an index of the efficiency of a reduced set of factors to account for the original variance.

3. Results

3.1. Overall Compositional Variation of FeMn Crusts

The concentrations of major and trace elements in the 57 FeMn crusts in this study show a large variation, providing the foundation for the hypothesis that crust composition will vary when distributed through a
large geographic area with different oceanographic conditions. Iron and Mn, which comprise the main mineral phases of FeMn crusts, each vary overall by 21 wt.%, ranging from 15 to 36 wt.% and having relative standard deviations (RSDs) of 22% and 26%, respectively (Table 2; supporting information Table S1; Mizell & Hein, 2019). Silicon and Al, which typically represent minor detrital phases found in FeMn crusts, exhibit overall ranges of 6.9 and 2.9 wt.% and have RSDs of 32% and 52%, respectively. Ba varies overall by 2,633 ppm, with a RSD of 37%. The RSDs for Cu, Cr, and Co are all above 60%, with Co exhibiting the largest overall range in concentration for the trace metals of 1.75 wt.%, from the minimum value of 0.14 to the maximum of 1.89 wt.% (Table 2).

3.2. Geographic Correlations Within the Data Set

Several of the geographic parameters being examined covary, which affects the proper interpretation of element correlations with those parameters. First, the MGT and HBT seamount chain transects are oriented northwest-southeast (Figure 1), and the magnitude of the change in latitude between sample locations along these two sample transects is much more than the change in longitude; therefore, zonal variations in crust composition within each of these individual sample transects are likely to be less significant than meridional variations or may be entirely caused by meridional controls. In addition, sample water depths anticorrelate with latitude within the whole data set ($R = 0.3801, n = 57$) and especially within the MGT transect ($R = 0.5863, n = 33$). Oxygen has a very strong correlation with water depth for the whole data set ($R = 0.9046, n = 57$) and even stronger for the primary MGT transect ($R = 0.9390, n = 33$). Therefore, element correlations with water depth and latitude may be mostly or completely attributable to correlation with oxygen concentration; however, we investigated each separately (Table 3).

3.3. Water Depth and Oxygen Correlations

CCM reveal positive Fe, Fe/Mn, and Cu correlations with water depth for the whole data set, MGT, and north of the equator but not within groups that are all or mostly south of the equator. The exception is Fe, which is also positively correlated with water depth in Samoa (Table 3; Tables S2 and S3). Si correlates with depth at the 95% CL for the whole data set and for the MGT transect. Barium correlates with water depth for the whole data set and MGT and north of the equator. Titanium shows positive correlations with water depth in the whole sample set, MGT, and south of the equator, which are the groups with the highest number of samples. Lead, Ni, and Co anticorrelate with water depth for the whole data set, MGT, and north of the equator, and one or more of Pb, Ni, and Co anticorrelate with water depth in most sample groups, except south of the equator. Zinc also anticorrelates with water depth in all of the sample groups that dominate south of the equator, except HBT, which is likely due to the small number of samples.

Despite oxygen and water depth being highly correlated, and many element correlations with these two parameters being similar, some element correlations with oxygen differ from those with water depth. Manganese, for example, shows a significant anticorrelation with oxygen for the whole data set, MGT, and Samoa, while Mn did not show significant anticorrelations with water depth in any of these sample groups. Al is correlated with oxygen for MGT but is not correlated with depth in any transect. Cadmium anticorrelates with oxygen for all samples, MGT, and groups south of the equator, including in HBT and the “MGT within HBT” groups. Sodium anticorrelates with oxygen for the whole data set and within MGT, but did not have significant correlations with depth in these transects.

3.4. Latitude Correlations

The Fe/Mn ratio anticorrelates with latitude (increases to the south) in all data groups except Samoa, HBT, and “MGT within HBT” (Table 3). Iron anticorrelates with latitude in MGT and in groups north of the equator and correlates with latitude south of the equator, whereas Mn correlates with latitude, especially for the MGT samples and even more strongly in the southern portion of the MGT transect. Cobalt, Mo, Ni, Pb, and sometimes V follow the behavior of Mn, correlating with latitude. Zinc correlates with latitude for all samples and MGT but anticorrelates with latitude south of the equator.

Silicon and Al anticorrelate with latitude overall and especially in the MGT transect samples, and Al also anticorrelates with latitude in all sample groups north of the equator. The Si/Al ratio, however, correlates with latitude in sample groups north of the equator and in MGT. Phosphorous is correlated with latitude...
Table 3
Tabulated Results From Correlation Coefficient Matrices Generated for Each of the Sample Groups

Latitude correlations

|                | All samples | MGT | Samoa | HBT | MGT within HBT | N. of equator | S. of equator | N. of equator (MGT) | S. of equator (MGT) |
|----------------|-------------|-----|-------|-----|----------------|---------------|---------------|---------------------|---------------------|
| n = 57 (+)     | (−)         | (+) | (−)   | (+) | (−)            | (−)           | (−)           | (−)                 | (−)                 |
| Pb             | Fe/Mn       | Pb  | Fe/Mn | Pb  | Fe/Mn          | Pb            | Pb            | Fe/Mn               | Pb/Mn               |
| Co             | Fe/Mn       | Pb  | Fe/Mn | Pb  | Fe/Mn          | Pb            | Pb            | Fe/Mn               | Fe/Mn               |
| Fe             | Mn          | Na  | Al    | Ca  | Cr             | Ba            | Co            | Pb                  | Pb                  |
| Ni             | Al          | Si  | Si    | Mn  | Cu             | Ca            | Ni            | Fe                  | Fe                  |
| Mn             | Na          | Ni  | Fe    | Pb  | Fe             | S/Al          | Al            | Cd                  | Cr                  |
| Na             | Pb          | Zn  | Mg    | As  | Na             | Ni            | Pb            | V                   | V                   |
| Mo             | Cr          | Ba  | Fe/Mn | Cd  | Pb             | Pb            | Pb            | Pb                  | Pb                  |
| As             | Cu          | Na  | V     | Cd  | Pb             | Pb            | Pb            | Pb                  | Pb                  |
| Cd             | Mg          | Fe  | S/Al  | Mo  | Ca             | Ni            | Pb            | Sr                  | Sr                  |

Longitude correlations

|                | All samples | MGT | Samoa | HBT | MGT within HBT | N. of equator | S. of equator | N. of equator (MGT) | S. of equator (MGT) |
|----------------|-------------|-----|-------|-----|----------------|---------------|---------------|---------------------|---------------------|
| n = 57 (+)     | (−)         | (+) | (−)   | (+) | (−)            | (−)           | (−)           | (−)                 | (−)                 |
| Pb             | Fe/Mn       | Pb  | Fe/Mn | Pb  | Fe/Mn          | Pb            | Pb            | Fe/Mn               | Pb                  |
| Fe             | Mn          | Na  | Al    | Co  | Al             | Pb            | Pb            | Pb                  | Pb                  |
| Fe             | Co          | Al  | Na    | Ti  | Mn             | Pb            | Pb            | Pb                  | Pb                  |
| Si             | Cr          | Cu  | Mn    | Y   | Mo             | Pb            | Pb            | Pb                  | Pb                  |
| Ti             | Mn          | Fe  | Mn    | Y   | Mo             | Pb            | Pb            | Pb                  | Pb                  |
| Y              | Pb          | Cu  | Ni    | Si  | Pb             | Pb            | Pb            | Pb                  | Pb                  |
| Cd             | Fe          | Cu  | Ni    | Si  | Pb             | Pb            | Pb            | Pb                  | Pb                  |

Water depth correlations

|                | All samples | MGT | Samoa | HBT | MGT within HBT | N. of equator | S. of equator | N. of equator (MGT) | S. of equator (MGT) |
|----------------|-------------|-----|-------|-----|----------------|---------------|---------------|---------------------|---------------------|
| n = 57 (+)     | (−)         | (+) | (−)   | (+) | (−)            | (−)           | (−)           | (−)                 | (−)                 |
| Pb             | Fe/Mn       | Pb  | Fe/Mn | Pb  | Fe/Mn          | Pb            | Pb            | Pb                  | Pb                  |
| Fe             | Mn          | Na  | Al    | Ca  | Cr             | Ba            | Co            | Pb                  | Pb                  |
| Ba             | Co          | Fe  | Co    | Ti  | Mn             | Pb            | Pb            | Pb                  | Pb                  |
| Ti             | Mn          | Fe  | Ni    | Cu  | Na             | Pb            | Pb            | Pb                  | Pb                  |
| Cu             | Mn          | Mn  | P     | Pb  | Pb             | Pb            | Pb            | Pb                  | Pb                  |

Oxygen correlations

|                | All Samples | MGT | Samoa | HBT | MGT within HBT | N. of equator | S. of equator | N. of equator (MGT) | S. of equator (MGT) |
|----------------|-------------|-----|-------|-----|----------------|---------------|---------------|---------------------|---------------------|
| n = 57 (+)     | (−)         | (+) | (−)   | (+) | (−)            | (−)           | (−)           | (−)                 | (−)                 |
| Pb             | Fe/Mn       | Pb  | Fe/Mn | Pb  | Fe/Mn          | Pb            | Pb            | Pb                  | Pb                  |
| Fe             | Mn          | Na  | Al    | Ca  | Cr             | Ba            | Co            | Pb                  | Pb                  |
| Ba             | Co          | Cu  | Co    | Ti  | Mn             | Pb            | Pb            | Pb                  | Pb                  |
| Ti             | Mn          | Fe  | Ni    | Cu  | Na             | Pb            | Pb            | Pb                  | Pb                  |
| Cu             | Mn          | Mn  | P     | Pb  | Pb             | Pb            | Pb            | Pb                  | Pb                  |
in sample groups that are located south of the equator. The HBT transect includes only nine samples, so very few element correlations are significant.

Singling out the MGT transect samples, different correlations occur when samples north versus south of the equator are included in the CCM. For example, Mn, Co, Ni, Zn, and Mo correlations with latitude are no longer observed when only MGT samples north of the equator are included. Whereas, Ti, V, Cd, and P correlate with latitude when just MGT samples south of the equator are included (Table 3).

### 3.4.1. Equatorial Upwelling Signal

Barium, Mg, and Fe all anticorrelate with latitude north of the equator and correlate with latitude south of the equator. The concentrations of Ba, Mg, and Fe are relatively high in FeMn crusts located within the EUZ compared to those outside the EUZ, which show a clear relationship with the high biological productivity in that region (Figure 3).

### 3.5. Longitude Correlations and Zonal Comparisons

#### 3.5.1. Correlations With Longitude From CCM

Within the whole data set, Fe correlates with longitude (more Fe to the east), whereas Mn, Pb, Co, Ni, and Mo anticorrelate with longitude (Table 3). For MGT samples, similar correlations are observed as with the whole data set, and As, Zn, and Si/Al additionally anticorrelate with longitude. In the Samoa region, Cr correl-ates with longitude while Cu anticorrelates with longitude.

#### 3.5.2. Comparison of Latitude, Water Depth, and Oxygen Correlations Within Zonally Offset MGT and HBT Transects

To further investigate changes in FeMn crust composition with longitude, we compared the element correlations with latitude, depth, and oxygen for HBT crusts to those of crusts from a subtransect of the MGT that is within the latitude range of and parallel to HBT but offset by approximately 8° of longitude. Within both samples of the MGT transect, different correlations occur when samples north versus south of the equator are included in the CCM. For example, Mn, Co, Ni, Zn, and Mo correlations with latitude are no longer observed when only MGT samples north of the equator are included. Whereas, Ti, V, Cd, and P correlate with latitude when just MGT samples south of the equator are included (Table 3).

### Table 3 (continued)

| Latitude correlations | All samples | MGT within HBT | N. of equator | S. of equator |
|-----------------------|-------------|----------------|---------------|--------------|
| Cd                    | As          | Mn             |               |              |
| As                    | Cd          |                |               |              |
| Mo                    |             |                |               |              |

Correlations at the 99% confidence level are in bold and correlations at the 95% confidence level are in italics; elements are listed from strongest to weakest correlation (highest to lowest absolute value).

Figure 3. The Ba (left), Fe (middle), and Mg (right) concentration at each dredge location, with the color darkening as concentration increases, overlying a map of surface chlorophyll-a concentrations (NASA 2019).
HBT and the subtransect of MGT, Ba correlates with latitude; however, in HBT, Mo also correlates with latitude, and Co anticorrelates with latitude, which is not seen in the MGT subtransect. The MGT subtransect reveals positive correlations for Fe and Mn as well as Mg, Ca, and P with latitude that are not seen in HBT. When element correlations with water depth and oxygen within these two regions are compared, Cd anticorrelates with water depth and oxygen in both regions. For HBT samples, Ca and Mg anticorrelate with oxygen and depth, while Ba correlates with both water depth and oxygen, none of which are observed in the MGT subtransect (Table 3). Lead and P anticorrelate with water depth oxygen in the MGT subtransect but not in HBT.

3.5.3. MGT Versus HBT Zonal Chemistry Trends

FeMn crusts from HBT contain more Fe and Mn than crusts from MGT within the same latitude range, but Fe/Mn ratios are similar, so the Fe and Mn enrichments are nearly equal (Figure 4). Generally, there is more Al in the samples from the MGT subtransect than in the HBT samples, but Si is similar. It is important to note that for the HBT transect and MGT subtransect, the distribution of samples with water depth and surrounding oxygen concentrations are fairly uniform, which means that zonal variations are likely independent of oxygen concentration in seawater. The exception is for the northernmost samples of this subset (~0°–1°N) where samples from the HBT transect are much deeper than the MGT samples at this latitude and are exposed to higher seawater oxygen concentrations; therefore, water depth and oxygen are likely controlling the Fe and Mn concentrations in these three samples (Figure 4).

3.6. Q-mode Factor Analysis of MGT

Q-mode factor analysis, based on the 33 samples within the MGT sample group, produced four factors that account for 93.8% of the variance, with Factors 1–4 accounting for 34.9%, 19.2%, 29.5%, and 10.3% of the variance, respectively (Table 4). The factor loadings for Factor 1 for each sample are correlated with oxygen at the 99% CL with an R value of 0.5870; however, the trend is not described entirely by oxygen concentration (Figure 5; note that the correlation appears negative since oxygen is decreasing to the

Table 4

Rotated VARIMAX Factor Scores for Elements Included in the Q-Mode Factor Analysis of Samples Within the MGT Transect

| Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|----------|----------|----------|----------|
| Pb       | K        | Y        | Ba       |
| Ni       | Si       | Ca       | Fe       |
| Co       | Al       | Si       | Mg       |
| Zn       | Ti       | Al       | Ti       |
| Mn       | Na       | V        | Mn       |
| Na       | Ba       | As       | V        |
| Mo       | Zn       | P        | Sr       |
| Cd       | Cu       | Sr       | Mo       |
| As       | Mg       | Fe       | Ca       |
| Y        | Fe       | Mo       | Y        |
| V        | Cr       | Cu       | As       |
| Sr       | Ni       | Cd       | Cd       |
| K        | Cd       | Cr       | Na       |
| Ca       | Mn       | Na       | Cu       |
| P        | Ca       | K        | Ca       |
| Ti       | Co       | Zn       | Pb       |
| Mg       | Pb       | Pb       | Cr       |
| Cr       | P        | Mn       | Co       |
| Cu       | Sr       | Co       | Al       |
| Ba       | V        | Mg       | K        |
| Si       | Mo       | Ni       | Ni       |
| Al       | Y        | Ti       | Si       |
| Fe       | As       | Ba       | Zn       |

Scores and associated elements are listed from highest to lowest score for each factor

Figure 4. Concentrations of elements in FeMn crusts as well as seawater oxygen concentrations at sample locations within the HBT transect (blue circles) compared to those from the subsection of the MGT transect (orange triangles) within the same latitude range of 2°N to 10°S.
Therefore, Factor 1 is interpreted to represent elements that vary due to the oxygen concentration in seawater at each sample location while recognizing that other influences are evident. Factor 1 describes the variance in the following elements, in order of decreasing factor scores, Pb, Ni, Co, Zn, Mn, Na, and Mo. Most of these elements, especially Ni, Co, and Mo, are known to be enriched in the Mn-oxide phase of FeMn crusts, so it is likely that when more Mn-oxide is precipitated in relatively lower oxygen concentrations, the other elements also become more enriched as they sorb onto the Mn-oxide phase.

Factor 2 is interpreted to represent a mixed influence of detrital input and increasing carbonate ion concentrations with water depth, since many of the elements with high factor scores for Factor 2 (Table 4) have significant correlations with water depth in CCM (Fe, Cu, and Si) or are elements typically associated with the detrital fraction of FeMn crusts (Si, Al, K, Na, Mg, Cr, and Zn). The factor loadings for each sample for Factor 2 have a weak but significant correlation (95% CL) with the estimated dissolved carbonate ion concentration at each sample location (Table S1; Mizell & Hein, 2019; Key et al., 2004; Figure 5). Colloidal Fe has been shown to be released during biogenic carbonate dissolution (Halbach & Puteanus, 1984; Palmer, 1985) and increased carbonate ion concentrations elevate pH and increase the oxidation rate of Fe(II) in seawater (King, 1998). In addition, Cu is highly enriched in the Fe-oxyhydroxide phase of FeMn crusts. Therefore, higher iron-oxide formation at depth where carbonate ion concentration is higher is a plausible interpretation for Factor 2. Silicon and Al have no relationship with carbonate ion concentrations yet have high scores for Factor 2. Detrital flux may also increase with depth due to weathering and mass movement of debris down the slopes of seamounts. Thus, Factor 2 likely reflects these two correlated depth-related phases.

Elements with high factor scores for Factor 3 include Y, Ca, Si, Al, Fe, V, As, Sr, and P (Table 4). The high factor scores for Si and Al indicate that like Factor 2, Factor 3 also partially represents detrital input to FeMn crusts. The plot of Factor 2 scores versus Factor 3 scores (Figure 5a) show that these factors are generally correlated (negative correlation) except for Si and Al, which supports that detrital inputs are distinguishing these factors. Additionally, the factor loadings for Factor 3 anticorrelate with latitude at the 99% CL. Latitude is interpreted here to indicate changes in detrital-associated elements (Si, Al, and K) and their ratios with latitude as presented in the previous section, which imply the possibility of differing detrital provenance or flux along the meridional transect (Table 3; see section 4). Due to the presence of P, Sr, V, As, and Y in this factor, a biogenic signal may also exist in this factor. The enrichment of these elements in seawater can be linked to high productivity and biogenic particle flux because they are bioessential elements (V and P) or preferentially sorb to organic matter (Sr, Y, and As).
Factor 4 is characterized by elements related by the EUZ, and factor loadings for each sample correlate at higher than the 99% CL ($R = 0.6757$, $n = 33$) with surface chlorophyll-a values (NASA 2019; Figure 5; Table S1; Mizell & Hein, 2019) at each sample latitude/longitude. The elements with the highest factor scores for Factor 4 in decreasing order are Ba, Fe, and Mg (Table 4), which were also the elements most strongly associated with the EUZ in CCM results (Table 3).

4. Discussion
4.1. Controls on the Major Oxide Phases

It is well established that thicker and more Mn- and Co-rich FeMn crusts are associated with proximity to OMZs due to the high dissolved Mn contents within the OMZ, and permissive depths for such metal-rich FeMn crusts have been described based on the depth of the OMZ (Cronan, 1984; Hein et al., 2000). This trait is well demonstrated by the sample transect here, which shows higher Mn and Co concentrations in the northern samples that were forming just below the lowest oxygen concentration observed in this region, at approximately 600–1,000 m water depth, which is the western portion of the Eastern Tropical North Pacific OMZ originating offshore of Mexico (Figure 2). The strong anticorrelation of Mn with seawater oxygen, as well as high scores for Mn in Factor 1 and correlations of Factor 1 loadings with seawater oxygen, substantiates that seawater oxygen concentration is the oceanographic property that has the most influence on Mn concentration in FeMn crusts (Table 3; Table 4; Figure 5). Unlike previous studies of crusts in the Pacific (e.g., Hodkinson & Cronan, 1991) that inferred OMZ locations from limited oceanographic data, this study uses measured oxygen concentrations interpolated to each sample’s specific location to account for fluctuations in oxygen concentration with depth as well as proximity to a stronger or weaker OMZ.

In contrast to Mn, Fe concentration as well as the Fe/Mn ratio in FeMn crusts in this study increase with water depth, as seen in many other Pacific Ocean crust compilation studies (e.g., De Carlo et al., 1987; Hodkinson & Cronan, 1991). The cause of increased Fe contents in crusts with depth is attributed to either a lessening contribution of Mn because crust growth is occurring further from the Mn-rich OMZ or a deep-water source of iron. Halbach and Puteaunus (1984) suggested that the increased dissolution of the carbonate tests of plankton with depth is a likely source of Fe to FeMn crusts. Additionally, kinetic experiments have shown that increased carbonate ion concentration in synthetic seawater increases the pH and increases the oxidation rate of Fe (II) in seawater (King, 1998). An increase in deepwater pH would also decrease the solubility of Fe (III), which has a solubility minimum around pH 8 (e.g., Liu & Millero 2002). These or similar pH-dependent processes could potentially also augment the Fe-(oxyhydr)oxide content in FeMn crusts. Dissolved carbonate ion concentrations correlate (95% CL) with the factor loadings of Factor 2, which has a high factor score for Fe. This suggests that the release of dissolved Fe from the dissolution of carbonate, and/or increased pH from high carbonate ion concentrations, leads to increased precipitation of Fe-oxyhydroxides in FeMn crusts. The carbonate compensation depth (CCD) in the equatorial Pacific is estimated at ~4,650 m in the modern Pacific and has risen to 4,100 m within the past 5 Myr (Pälike et al., 2012), which is the average age of the upper layers of FeMn crusts in this study as calculated from their estimated crust growth rates (average 3.14 mm/Myr) using the cobalt-based chronometric equations of Manheim and Lane-Bostwick (1988); growth rate calculations discussed further in 4.1.1. The mean depth of samples in this study is 2,900 m with a maximum depth of 4,354 m; therefore, none of the samples occur below the modern CCD, and only four occur below the paleo CCD of 4,100 m. However, the dissolved carbonate ion concentration in this region of the modern ocean nonetheless generally increases with depth below 2,000 m because of deep and bottom waters that are more recently ventilated. This argues in favor of a pH-dependent process rather than the dissolution of biogenic carbonate tests as a more likely source of the correlation between Fe and depth.

Isotopic studies reveal that hydrothermal emissions and sediment redox cycling can be significant sources of Fe to the deep ocean (Horner et al., 2015), which may also explain increased Fe contents in FeMn crusts with depth. The trace element composition of water masses in the Indian Ocean show that Fe concentration in seawater is elevated in deep waters due to hydrothermal contribution at specific depths (Nishioka et al., 2013), and Hein et al. (2016) attributed increased Fe concentration in FeMn crusts from the same depths along the Ninetyeast Ridge to their growth from this Fe-rich Indian Ocean water mass. However, the region studied here does not have a hydrothermal source that is likely to supply the entire line of seamounts at a
consistent depth; only the southern portion of the sample region is close enough to known hydrothermal sources (Tonga-Kermadec Arc and Back-arc), but the depth trend for Fe is consistent for all crusts in the region. Also, a proxy to determine whether dissolved carbonate ion concentrations or hydrothermal input is the dominant contributor to enriched Fe concentration in FeMn crusts, that can be interpreted using bulk element concentrations of FeMn crusts alone, is not known.

A third explanation for an increase in Fe content in FeMn crusts with depth is increased entrained detrital material. As seen in the CCM results (Table 3), Si also increases with depth and both Si and Al, which are detrital elements, have strong factor scores in depth-related Factor 2 of the Q-mode factor analysis. Iron is a major component of the majority of the aluminosilicate minerals found in the deep ocean; therefore, if detrital input to FeMn crusts is increasing with depth, Fe concentration should also increase. Detrital input to crusts likely increases with depth due to the downslope movement of materials as the seamounts are eroded and debris is reworked. However, mass-balance calculations for Fe associated with the estimated detrital contribution to total FeMn crust mass do not favor this source for most of the increased Fe (Hein et al., 2003). The ultimate cause of the increase of Fe in FeMn crusts with water depth is likely associated with all of these factors; however, in this study, we are only able to test the dissolved carbonate ion concentration hypothesis quantitatively, and we determine that it is consistent with our data.

### 4.1.1. Fe and Mn Associated Elements

Most of the trace elements analyzed in this study have a typical association with either the Mn-oxide or Fe-oxyhydroxide phases in FeMn crusts based on their speciation in seawater, and these associations have been substantially confirmed by sequential leaching studies (Koschinsky & Halbach, 1995; Koschinsky & Hein, 2003). Cobalt and Ni are strongly associated with the Mn phase in crusts throughout the global ocean, and both follow the geographic and oceanographic correlations of Mn in this study. Notably however, the anticorrelations of Ni and Co with water depth are significant at the 99% CL, while Mn was not anticorrelated with water depth at even the 95% CL. Manganese might be expected to anticorrelate with water depth in the Pacific, however, since oxygen concentrations are lower at shallower depths. The fact that Co and Ni show strong anticorrelations with water depth independent of Mn but the same strong anticorrelations with oxygen as Mn, suggests that Co and Ni either experience additional water depth-related controls on their concentration in crusts, or their enrichment is not as strongly controlled by oxygen concentrations in seawater as for Mn. Cobalt has a scavenged-type vertical profile in the Pacific Ocean, while Ni has a nutrient-like vertical profile on average in the Pacific (Bruland, 1983). However, both Co and Ni have fairly uniform concentrations in seawater below ~1,500 m where the crusts studied here occur, so metal supply is not the cause of the discrepancy between Mn and Ni and Co with water depth. The high Co enrichment in FeMn crusts has been explained by its surface oxidation from Co$^{2+}$ to less soluble Co$^{3+}$ at the surface of crusts; however, this has not been identified as a surface reaction for Ni (Hein et al., 2000; Hem, 1978; Manceau et al., 1997). The probable control for both the Ni and Co concentrations is the growth rates of the crusts. Growth rates tend to increase with water depth in general, and therefore, crusts with slower growth rates commonly occur at shallower depths and have higher Co and Ni concentrations (Halbach & Puteanus, 1984; Hein et al., 2000). Growth rates estimated for FeMn crusts in this study using the Manheim and Lane-Bostwick (1988) equations do anticorrelate strongly with Co and even more strongly with Ni ($R = -0.6914$ and $-0.8028$, respectively, for $n = 57$). While these growth rates are estimates and would be more informative if calculated from absolute ages determined by isotope measurements, these results do indicate that slower growth rates at shallower depths allow for increased accumulation of Ni and Co. This change in growth rate with water depth has been clearly verified for continental-margin crusts (Conrad et al., 2017) and has been inferred to also characterize open-ocean crusts but may not always be invariably true. For example, Usui et al. (2017) showed that growth rates of crusts do not change with water depth over a detailed sampling from the base to the summit of a West Pacific seamount. However, the data presented here support that growth rates in FeMn crusts do change with water depth in Pacific open-ocean crusts and that growth rates also affect the accumulation of Mn-oxide associated elements.

Zinc and Mo also have the same geographic and oceanographic correlations as Mn, and Cu and Ti align with those of Fe, which are expected phase associations based on element correlations, sequential leaching, and/or X-ray absorption studies, and confirm that the concentrations of these trace elements are controlled by the amount of the major oxide to which they sorb (Hein et al., 2003; Kashiwabara et al., 2011; Koschinsky & Hein, 2003). Lead and As, however, are thought to dominantly associate with the Fe-oxyhydroxide phase...
based on sequential leaching (Koschinsky & Hein, 2003) but instead correlate at the 99% CL with Mn and follow the geographic and oceanographic correlations of Mn in CCMs for all samples and for samples within the MGT transect. Lead has a very short residence time in seawater (Flegal & Patterson, 1983), so local and temporal changes in dissolved Pb distribution in the water column can affect its concentration in FeMn crusts. Dissolved Pb data from the Pacific equatorial region shows a strong subsurface maximum from 20°N to 50°N at the 160°W meridian, attributed to aerosol material that sinks just fast enough to avoid scavenging by biogenic particles in the surface and is then distributed to the equatorial region via the subtropical gyres (Zheng et al., 2019). This suggests that modern increased concentrations of Pb in the subsurface from leaching of eolian dust along the northern portion of the sample region, that coincidentally mirror those of Co and Mn due to the stronger OMZ in the north, can explain the grouping of Pb with the geographic-oceanographic correlations of Co and Mn in this study. Additionally, Pb does show statistical correlations with both Mn and Fe in other regions of the Pacific (Hein et al., 2003), and the surface binding mechanisms allows for sorption of Pb to both the Fe and the Mn phase, as demonstrated by Takahashi et al. (2007).

Arsenic has a nutrient-like distribution in the Pacific, with little fluctuation in concentration from 1,000–5,000 m water depth, so variation in the concentration of As in crusts is not due to changes in the As supply throughout the water column (Cutter & Cutter, 2006). Arsenic in seawater is most commonly in the form of As(V) arsenates (e.g., H2AsO4⁻/HAsO4²⁻/AsO4³⁻; Byrne, 2002), and As in FeMn crusts was confirmed with X-ray absorption spectroscopy to also have an oxidation state of As(V) (Kashiwabara et al., 2008). Therefore, the oxidation of As at the surface of the Mn oxide is not a likely mechanism for its association with Mn in the FeMn crusts here. However, As(V) arsenates can adsorb to Mn (IV) vacancy sites of synthetic Mn-oxides (Foster et al., 2003), which may be a reaction occurring here, or As may accumulate through coprecipitation reactions, either of which need to be confirmed using micro X-ray absorption spectroscopy. The elements Ti, Cd, Cr, V, and Y did not show consistent correlations with the oceanographic and geographic properties analyzed in this study and therefore are not discussed.

4.2. Productivity Signatures

Barium, Fe, and Mg show significant increases in concentration within the EUZ region, and thus, their concentrations appear to be linked to surface productivity (Figures 1 and 3). Barium in FeMn crusts is dominantly found in the Mn-oxide phase during sequential leaching of nonphosphatized crusts, thus Ba is likely sorbed to the Mn-oxide phase as a hydrated cation, Ba²⁺ (Koschinsky & Hein, 2003). Throughout the open ocean, dissolved Ba has a nutrient-like distribution and is thus dominantly controlled by biological uptake in surface waters and subsequent release during remineralization of biogenic debris as it sinks to deeper waters (Chow & Goldberg, 1960; Paytan & Kastner, 1996), so the general increase of the biogeochemical cycling of Ba in the EUZ may provide increased dissolved Ba to FeMn crusts there. In addition, particulate barite flux to the deep ocean is increased when the productivity of overlying surface waters increases (Dymond et al., 1992). Although barite is not a major contributor to FeMn crust mineralogy, individual micrometer-scale barite grains are often seen using SEM analysis of FeMn crusts, so particulate barite can provide a small component of the increased Ba contents in crusts. Further, Paytan and Kastner (1996) found that, although sedimentary barite has low solubility, there is flux of dissolved barium to benthic waters from barite dissolution in oxic sediments in areas of high surface productivity, which may also supply dissolved Ba to FeMn crusts in the EUZ. Thus, the increased Ba content in FeMn crusts in the EUZ is reasonable and can be expected for similar regions of elevated productivity.

Iron is also highly associated with biogenic flux to the deep ocean; it is a micronutrient for most plankton so is taken up at the surface. Because it is particle reactive, only a portion is released back to the dissolved iron pool during remineralization of sinking biogenic particles, and the rest is scavenged back onto sinking particles (Twining et al., 2014). The EUZ, specifically, is a region of high productivity and has a highly efficient biological pump with particles raining at a high rate to the deep ocean (Kiko et al., 2017). The EUZ also receives high dissolved iron from the equatorial undercurrent originating from the Western Pacific (Slemons et al., 2010). Biogenic and scavenged iron may thus be efficiently transferred from the relatively high iron supplied from the equatorial undercurrent to regions of FeMn crust formation in the EUZ.

Increased Mg in FeMn crusts below the in EUZ region is less straightforward. Dissolved Mg is highly concentrated in ocean water, has a conservative profile with depth, and occurs mostly as Mg²⁺ in the dissolved phase, which sorbs to the surface of negatively charged MnO₂ (Koschinsky & Hein, 2003); however, Mn is
not more highly concentrated in crusts from the EUZ region (discussed below). Magnesium has been shown to preferentially sorb to the surface of biogenic opaline sediments over the other major cations, Na and K, in some regions of the equatorial Pacific (Donnelly & Merrill, 1977), and diatoms, which have opaline frustules, can dominate the phytoplankton population in equatorial divergence zones, such as the Pacific EUZ examined here (Estrada et al., 2016). Therefore, one possible explanation for the enrichment of Mg in FeMn crusts below the EUZ is biogenic opal flux to deep waters and Mg desorption/sorption from opaline sediments to nearby FeMn crusts. Alternatively, Mg is also moderately high in the easily leached phase of FeMn crusts, which is predominantly carbonates (Koschinsky & Hein, 2003), and Mg is incorporated into the calcite tests of foraminifera and nanoplanckton. Thus, increased Mg in these FeMn crusts may also reflect greater amounts of carbonate tests incorporated into them as marine snow during their slow growth below the productive surface waters of the EUZ.

Phosphorous flux to the deep ocean from the degradation of sinking organic matter is greater in regions with high surface productivity, and P is highly scavenged by Fe-oxyhydroxide particles (Filippelli & Delaney, 1996). However, P concentrations are not elevated in the FeMn crusts in the study region below the EUZ, as might be expected. P does correlate with Fe for all samples (99% CL) and within the MGT transect (95% CL); however, P concentrations in the FeMn crusts do not correlate with the phosphate concentrations in seawater (Garcia et al., 2014b; Table S1; Mizell & Hein, 2019) at each sample location within the primary MGT transect. The decoupling of P concentration in crusts and productivity occurs throughout the central Pacific (Hein et al., 2000) and requires further investigation into the surface chemistry of P in FeMn crusts and the controls on the accumulation of P in nonphosphatized crust layers.

**4.2.1. Basin-Wide Versus Regional Characteristics**

Hodkinson and Cronan (1991) compiled data for FeMn crusts from much of the Pacific Ocean (~25°N to ~25°S and 175°E to 150°W) and reported general trends in the chemical composition of crusts with location. For that large area, some correlations differed from our results. Most strikingly, Hodkinson and Cronan (1991) found that Mn increased near the equator which they attributed to surface productivity due to equatorial upwelling. In contrast, when restricted to our specific sample region and with more detailed sampling of the younger, uppermost crust layers, it was Fe, not Mn, that was more enriched within the EUZ. Although there is a subsurface minimum in oxygen along the EUZ when sinking organic matter is respired below the photic zone, subsurface EUZ oxygen concentrations are not low enough to strongly affect Mn concentrations in the FeMn crusts for the sample area examined here. The Mn trend observed by Hodkinson and Cronan (1991) was due to the strong OMZs further east in the tropical Pacific, including the poorly ventilated Eastern Tropical Pacific oxygen deficient zones, that propagate westward from the west coasts of Mexico and Peru.

These regional variations show that a more nuanced view of environmental conditions is required for choosing regions of interest for potentially economic FeMn crusts. While the larger-scale studies point to the equatorial region for higher Mn and therefore more Co-rich crusts (Co being the main metal of economic interest in crusts), it is clear from this study that for island nations looking for resources within their Exclusive Economic Zones, shallower-water crusts from the northern subtropical region should be the area of focus in order to collect FeMn crusts growing beneath or near the strongest modern OMZ. In addition, for FeMn crust exploration in areas beyond national jurisdictions and for thicker crusts from older seamounts, current OMZs as well as past OMZ reconstructions can be used to locate the most Mn- and Co-rich bulk crusts.

**4.3. Detrital Sources Interpreted From Bulk Compositions**

Sourcing the detritus in FeMn crusts is best done by isolating the detrital fraction of the crust material using reductive leaches of the Fe- and Mn-oxide phases and then measuring element (Pb, Nd, Hf, and Sr) isotopes of the detrital material (e.g., Dausmann et al., 2015). However, this process requires large amounts of sample material, chemical reagents, and time, so it is useful to understand how much detrital source information can be interpreted from the bulk chemical composition of FeMn crusts. Silicon, Al, and especially Si/Al ratios have been used as the signature elements of the detrital phase in FeMn crusts not only because they are the major components of most terrestrial detritus, such as clays, feldspars, and quartz but also based on correlations, factor analyses, and sequential leaching studies of FeMn crusts (Hein et al., 2000). Silicon and Al consistently anticorrelate with Mn, and are grouped in factor analyses with other elements that make up detrital minerals, like K, Mg, Ca, Cr, Zn, Li, Cs, and/or Se (Hein et al., 2000; Hein & Koschinsky, 2014). The
other major elements found in aluminosilicate minerals, like Mg, Ca, and K, are used in ratio to Al and Si to discriminate type and source of detritus in marine particles and sediments; however, in bulk FeMn crust samples, this method can be confounded due to the fact that Mg, Ca, and K cations can sorb to the negatively charged Mn-oxide surfaces of FeMn crusts. Therefore, an undetermined portion of their concentration in bulk crusts is due to sorption, and only the remaining portion comprises their contribution from aluminosilicate minerals. However, in this study, K did not correlate well with Mn or Fe ($R$ is 0.2100 and 0.0877, respectively for $n = 57$) and normalizing K to the sum of Fe and Mn concentrations did not improve the efficacy. Thus, we have used K as a third element in conjunction with Si and Al to aid in determining the variance of detrital sources along our sample transect, although we acknowledge that the absolute concentrations of K, and even Si and Al, can be influenced by sorption of their dissolved species onto the charged surfaces of the oxides.

A ternary plot for Si, Al, and K concentrations (K multiplied by 10 to spread out the data) for all of the samples in this study shows that the FeMn crust samples align along a linear trend coinciding with their location along the meridional transect (Figure 6). The northernmost samples (Gilbert) plot at the highest K and low Al region of the line, followed by the HBT samples; Gilbert and Tuvalu intermix next along the linear progression, and Samoa completes the line toward the highest Si and higher relative Al section of the ternary plot. Although these values cannot be directly compared with the Si, Al, and K concentrations and ratios of potential source detritus due to the dilution and sorption factors in FeMn crusts discussed, it is clear from the linear separation that the detrital sources in the crust do vary from the northern to southern ends of the sample transect. This result was corroborated by the Q-mode factor analysis in which Factor 3, interpreted to partially represent detrital flux and provenance, showed a strong correlation of factor loadings with latitude. Latitude is not an actual proxy for detrital provenance or flux; thus, further evidence that detrital sources vary along the meridional transect in this region follows.

The Si and Al absolute concentrations in crusts both decrease toward the north for all samples and within the MGT group (99% CL anticorrelations with latitude); however, the Si/Al ratio increases toward the north (95% CL within the MGT transect), which indicates that although more detrital material is being delivered to the southern portion of the MGT transect, more silica-rich detritus characterizes the crusts to the north. However, when the Si/Al ratios for the entire sample set are considered with respect to latitude, the Samoa samples have Si/Al ratios similar to those of the mid to north sectors of the MGT transect, suggesting that a silica-rich, aluminum-poor detrital source also prevails near Samoa (Table S1; Mizell & Hein, 2019). Average loess from New Zealand has the highest Si/Al value of any of the potential detrital sources to this region (4.30; Taylor et al., 1983) followed closely by the average loess from China (4.25; Gallet et al., 1996), which could indicate that the northern and southern segments are supplied by more Si-rich wind-blown detrital material from the closest dust sources, yet 25 of the 57 FeMn crust samples have Si/Al that are still higher than the loess values. These high Si/Al ratios are likely caused by low Al concentrations. Three samples within the HBT sample group had especially low Al values of less than 0.01%; these may be errors in the analytical data, and we will not emphasize those data here. Some samples may also be slightly enriched in Si due to the sorption of dissolved silicate to the slightly positively charged Fe-oxyhydroxide phase, although Si concentrations in the crusts do not correlate with dissolved silicate concentrations in the seawater at each sample location within the primary MGT transect (Table S1; Mizell & Hein, 2019; Garcia, et al., 2014b).

The majority of the Tuvalu and Gilbert crust samples have lower Si/Al ratios (average 3.95 and 3.67, respectively) that are closer to basaltic source rocks, such as average ocean island basalt (3.37; Dasgupta et al., 2010), Samoa Island basalt (3.33; Dasgupta et al., 2010), and average oceanic arc basalt (2.80; Arculus, 1981).Several samples from the Gilbert Islands clump at the lowest end of the Si/Al spectrum (minimum 1.12), which are closest to tholeiitic basalts from seamounts of the Tonga-Kermadec Arc (2.09; Brothers...
et al., 1980); however, this detrital source is unlikely due to the large distance between the Gilbert Islands and the Tonga-Kermadec Arc. The low Si/Al ratios seen in the Gilbert chain occur within the EUZ, which suggest that perhaps higher Al is being delivered to crusts here due to biological particle flux to the deep ocean as observed by (Murray & Leinen, 1996). Conversely, the adjacent HBT samples are also situated within the EUZ and have the highest Si/Al ratios. The high Si/Al ratios in the HBT samples are supported by the 95% CL correlation of excess silica (Siex) for each crust sample in the EUZ (Table S1; Mizell et al., 2019; calculated based on the Si/Al ratio for average ocean island basalt; 3.37; Dasgupta et al., 2010) with corresponding surface chlorophyll-a values ($R = 0.8113$, $n = 10$; Figure S1). Increased biogenic silica input to FeMn crusts within the EUZ, especially for the HBT samples where surface productivity is the highest for the entire data set (Figure 1), may explain the Siex beyond the proposed detrital inputs. These data demonstrate that bulk major element concentrations in crusts along these transects have complex local distributions that make it difficult to constrain specific detrital sources.

## 5. Summary and Conclusions

The uppermost layers (<15 mm) of 57 FeMn crusts along a linear chain of seamounts in the western equatorial Pacific, from 14°N to 14°S, show a wide variation in the concentrations of 23 major and trace elements, and the majority of the compositional variation can be attributed to several key modern oceanographic and geographic characteristics in the region. Oxygen concentrations throughout the water column control variations in FeMn crust composition with both latitude and water depth. Meridional changes in oxygen concentration are predominantly due to the presence of a stronger OMZ in the northern subtropical portion of the sample area, while depth controls are caused by the stratified, increasing oxygen concentrations with depth. The oxygen concentration of seawater has the strongest influence on Mn concentration in FeMn crusts. Mn concentrations anticorrelate with dissolved oxygen at the 99% CL at each sample location. Q-mode factor analysis of samples along the main MGT transect produced an oxygen-related factor with a high factor score for Mn; both of these quantitative statistics linking Mn content in FeMn crusts to seawater oxygen concentration are presented here for the first time. Elements known to associate with the Mn-oxide phase of FeMn crusts, like Co, Ni, Mo, and Zn, all exhibit similar geographic-oceanographic correlations as Mn. However, Co, Ni, and Zn are not as sensitive to oxygen concentrations as Mn, and they have significant anticorrelations with water depth that are attributable to increasing growth rates with water depth, which Mn does not.

The iron content of FeMn crusts in this study increases with water depth, which has been attributed to the following factors in previous works: decreasing Mn concentrations in the crust with increasing oxygen concentrations in seawater at depth, increased dissolved Fe concentrations in seawater with depth due to the dissolution of carbonate particles, deep hydrothermal sources, release from sediments, and increases in Fe-bearing aluminosilicate detritus. Q-mode factor analysis in this study shows a factor with a high Fe factor score for which dissolved carbonate ion concentrations at each sample location correlate at the 95% CL with factor loadings. This result offers the first quantitative statistic to support the hypothesis that an increase in carbonate ion concentration with increasing water depth from younger water masses or biogenic carbonate dissolution can increase the Fe content of FeMn crusts with increasing water depth. We attribute this mainly to increased pH with increased carbonate ion concentration. However, we acknowledge that deep Fe sources as well as decreasing Mn precipitation also contribute to this increase in Fe with water depth. Copper, and in some cases Ti, have higher concentrations when Fe concentration is higher, as expected, due to their preferential enrichment in the Fe-oxyhydroxide phase of FeMn crusts. Lead, on the other hand, can be enriched in the iron phase, but instead has the same geographic-oceanographic correlations as Mn. The variance in Pb content in FeMn crusts in this region may be attributed to local fluctuations in seawater concentrations, which is a unique characteristic among the trace elements reported here.

The higher surface productivity seen within the EUZ (~5°N to ~5°S) is another meridional control on FeMn crust composition in this region, causing elevated Fe and Ba concentrations in crusts due to their association with efficient biogenic particle flux, which transports elevated Fe and Ba to depth where it can be incorporated into FeMn crusts. Magnesium is also more concentrated in FeMn crusts within the EUZ region, and the cause of its enrichment is likely the result of higher flux of Mg-rich carbonate and opal particles as marine snow.
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