ORIGINAL RESEARCH PAPER

Fine-scale compositional variations in a Co-rich Mn crust from the Marcus-Wake Seamount cluster in the western Pacific based on electron microprobe analysis (EMPA)

Xiangwen Ren · G. P. Glasby · Jihua Liu · Xuefa Shi · Jingwu Yin

Received: 21 November 2006/Accepted: 20 May 2007/Published online: 30 June 2007 © Springer Science+Business Media B.V. 2007

Abstract The internal structure and composition of a 37mm-thick Co-rich Mn crust from the Lamont Guyot in the Marcus-Wake Seamount cluster have been studied in detail by means of electron-probe microanalysis (EPMA). 184 point analyses for 16 elements were carried out at an average spacing of 0.20 mm and each point was dated using the Co-geochronometer method. Two types of variation in composition were observed in the crust: long-term trends and short-term erratic variations. The long-term trends were identified using the fifth order polynomial. Mn and Ni were shown to increase in concentration from 23.3 Ma to a maximum at about 20 Ma and then decline steadily to the Present, whereas Fe, P and Si showed the opposite trend. By contrast, Co displayed a double humped pattern with maxima at about 19 Ma and 3.5 Ma and minima at 23.3 Ma, about 11 Ma and at Present. The longterm trends in element concentrations in the crust lead us to suggest that much of the Fe in western Pacific Ocean ferromanganese crusts is aeolian in origin and derived from the deserts of central Asia. Cooling of the Asian mainland at about 20 Ma led to an increase in the flux of Fe to the oceans. This was supplemented by an additional input of Fe into the crusts as a consequence of the dissolution of biogenic CaCO₃ tests at 4.5-10.5 Ma. For the short-term erratic variations, three periods of 0.61, 0.96 and 1.65 m.y.

X. Ren · G. P. Glasby · J. Liu · X. Shi (⊠) Key Laboratory of Marine Sedimentology and Environmental Geology, First Institute of Oceanography, State Oceanic Administration, No. 6 XianXiaLing Road, High-Tech District, Qingdao 266061, P.R. China e-mail: xfshi@fio.org.cn

J. Yin

Geological Laboratory Center, China University of Geosciences, 29 Xueyuan Road, Beijing 100083, P.R. China

were identified by spectral analysis. The second harmonics of these periods are 1.22, 1.92 and 3.30 m.y., which may correspond to the highest-order periods for eccentricity of 1.31, 2.04 and 3.47 m.y. This suggests the possibility that the high-frequency oscillations of the time series data are linked to climatic changes controlled by the highest-order periods of the Milankovitch cycles.

Keywords Co-geochronometer · Co-rich manganese crust · Electron microprobe analysis · Lamont Guyot · Marcus-Wake Seamount cluster

Introduction

Co-rich Mn crusts may be considered to be condensed stratigraphic sections that record variations in paleoceanographic conditions with time. As a result, they have attracted considerable attention over the past 10–15 years for the study of the patterns of deep ocean circulation and to establish the provinciality of the crusts. These studies have been mainly based on the determination of the distribution of the long-lived radiogenic isotopes of Nd, Pb, Be, Hf and Os in well-dated crusts. This topic was well reviewed by Frank (2002). However, relatively few studies have been directed to the study of the fine scale internal structure of Co-rich Mn crusts, which underpins the interpretation of these paleoceanographic data.

The use of electron microprobe analysis (EMPA) to study variations in the composition of Co-rich Mn crusts with depth in the crust has been reported by Hein et al. (1992), Jeong et al. (2000) and Frank et al. (1999). In particular, Hein et al. (1992) studied a 47- to 60-mm thick crust from the Horizon Guyot in the central Pacific. The age of this crust was estimated to be 18.5 Ma by ⁸⁷Sr/⁸⁶Sr

dating, based on comparison with the standard seawater Sr isotope curve. EMPA was carried out at 1 mm intervals at 50 locations on a vertical profile through a polished section of the crust. 16 elements were analyzed at each location and profiles of the element distribution were plotted. Optical studies on the polished section suggested that botryoidal layers formed during hiatuses in crustal growth when ocean bottom water flow intensified and laminated intervals formed during more quiescent periods of bottom water flow. Broad changes in the composition of the crust with time (at 15, 11.5, 7.4, 6.4, 5.2 and 4.6 Ma) were thought to be related to changes in the pattern of ocean circulation (Hein et al. 1992). Highfrequency changes, on the other hand, were thought to be related to Milankovitch orbital parameters corresponding to the highest-order periods for eccentricity at about 3.47, 2.04 and 1.31 m.y.

Jeong et al. (2000) studied seven Co-rich Mn crusts from seamounts located in the Marshall Islands, Micronesia and the Palau Islands. The crusts from the Marshall Islands were shown to be much thicker (54–104 mm) than those from Micronesia and Palau Islands (15–42 mm) and displayed two generations of crustal growth, an older generation characterized by impregnation of CFA (carbonate fluorapatite) in compact laminations and columns and younger crust characterized by porous botryoidal and columnar structures. The boundary between these two generations was dated at about 25 Ma. In samples from Micronesia and the Palau Islands, only the younger generation of the crusts was present.

On a much shorter time scale, Han et al. (2003) radiometrically dated the outer 1.3 mm of a deep-sea manganese nodule from the Clarion-Clipperton Fracture Zone in the equatorial North Pacific by means of the ²³⁰Th/²³²Th method at 0.1 mm intervals and presented evidence that the occurrence of laminae bands in the nodule is controlled by Milankovitch cycles related to orbital eccentricity (95 and 123 k.y.), obliquity (41 and 54 k.y.) and precession (23 and 19 k.y.), respectively. These authors also suggested that Pacific deep-sea nodules may have been constructed by numerous microbes with filaments about 2-4 nm in diameter. Assuming that these microbes reproduce once or twice per year, it was estimated that this would correspond to a growth rate of the nodule similar to that determined for this nodule (4.6 mm m.y.⁻¹). However, the size attributed to these microbes is much smaller than the diameter of 100 nm by which nannobacteria are defined and is considered by many to be below the size limit for viable living organisms (Nealson 1997). In addition, Melnikov and Pulyaeva (1995) have compared the characteristics of Corich Mn crusts from the Marcus-Wake and Magellan Seamount clusters and shown that the Marcus-Wake Seamount crusts are thinner but contain higher concentrations of Mn and Co and lower concentrations of P than the Magellan Seamount crusts.

In this study, we present the results of a detailed electron microprobe study of a Co-rich Mn crust from the Marcus-Wake Seamount cluster in the western Pacific Ocean in order to investigate further some of the interesting ideas presented by previous workers.

Sample description

The sample investigated in this study is a 37-mm-thick Corich Mn crust (L09-A-1), which was dredged by R/V Dayang Yihao from Lamont Guyot in the Marcus-Wake Seamount cluster at 21°28'N, 159°40'E at a water depth of about 2450 m. Figures 1 and 2 show the location of the Lamont Guyot in the Marcus-Wake Seamount cluster.

In polished section, the crust can be divided into four intervals (Fig. 3). The upper interval (0-10 mm) corresponding to an age of 0-7.6 Ma (see below) was black with a columnar texture. The second interval (10-28 mm), corresponding to an age of 7.6-18.5 Ma, displayed an irregular dendritic texture and was streaked by vertical bands of light-coloured detrital material about 5 mm wide. The third interval (28-34 mm), corresponding to an age of 18.5–22.5 Ma, was also black and characterized by a dense dendritic texture. This consisted of irregular V-shaped structures about 2-8 mm wide growing upwards and separated from each other by cracks about 2 mm wide. These cracks were infilled by light-coloured detrital material. The individual columns within these V-shaped structures are about 350 µm wide and continuous throughout the interval. The lowermost interval (34-37 mm), corresponding to an age of 22.5-23.3 Ma, was too thin to enable a proper description at the macroscopic level except that it formed an irregular contact with the underlying substrate. The substrate was a breccia made up of highly-weathered finegrained silicate debris (typically < 1 mm in diameter). The matrix of the breccia had been significantly interpenetrated by manganese oxides.

Studies of backscattered electron images of a polished section of the crust showed that the upper interval (0–10 mm) of the crust consisted principally by columnar growth structures typically about 3000 μ m long and 500 μ m wide, which were characterized by the presence of rhythmic fine banding, with the finest bands about 1 μ m wide. The second interval (10–28 mm) displayed a dendritic texture with columns typically about 500 μ m wide and containing a much higher detrital mineral fraction than the upper interval. This interval was characterized by the occurrence of two types of cracks; (1) sharper cracks with a width of about 60 μ m formed as a result of dehydration of the crust after collection and (2) more diffuse cracks with a

Fig. 1 Schematic map showing the location of the Marcus-Wake Seamount cluster. The location of the Co-rich Mn crust studied by EPMA is indicated by a black filled star. The location of the crust at 23.3 Ma was estimated by assuming that the underlying Pacific Plate had migrated at a rate of 70 mm a^{-1} in a direction of 290° for the past 23.3 Ma. This location is indicated by a black filled circle





219

1599

159°30'



Within this section, there appear to be no major hiatuses and no evidence of the botryoidal and laminated intervals recorded by Hein et al. (1992). In particular, the boundaries between the intervals do not appear to represent hiatuses because they are not associated with any enrichments of aluminosilicates, CFA (carbonate fluorapatite) or biogenic calcite. It should be noted that, in this section, the columnar growth structures are all aligned in the direction of crustal growth whereas the fine cracks are aligned parallel to the layering of the crust.

160°30'

Analytical methods

160°

Electron-probe microanalysis of the Co-rich manganese crust was carried out at the Geological Laboratory Center of the China University of Geosciences in Beijing. For this

21

161°

Fig. 3 Profile of the polished section of the Co-rich Mn crust studied by EPMA. The crust could be divided into four intervals; the upper interval (0-10 mm) corresponded to an age of 0–7.6 Ma: the second interval (10-28 mm) to an age of 7.6-18.5 Ma, the third interval (28-34 mm) to an age of 18.5-22.5 Ma and the lowermost interval (34-37 mm) to an age of 22.5-23.3 Ma. Variations in the Mn/Fe ratios of the crust are plotted as a solid line and in the Si/Al ratios as a dashed line. The ages of the stratigraphic intervals in the crust and of major paleoceanographic events during the last 23.3 Ma are shown as horizontal lines



purpose, a section was cut vertically through the crust and one side was polished. The polished section was then attached to a micro slide with resin and the other side polished to produce a thin section. The thin section was then placed in a SC701C Quick Carbon Coater and coated with a film of carbon. The sample was analyzed using an EPMA 1600 electron-probe microanalyzer manufactured by Shimadzu of Japan. Prior to analysis, the thin section was placed in the vacuum chamber of the electron-probe microanalyzer and the air contained in the pores of the crust driven out by vacuum pump. The acceleration voltage, beam current and the diameter of the spots analyzed in this study were 15 ky, 7 nA and 10 µm, respectively.

The EMPA measurements were carried out for 16 elements including O and the results are expressed in per cent. All the elements except Cl are present in the crust as oxides. The concentration of H was calculated on the assumption that H occurs in the crust as H₂O and balances any residual O left over. It should be noted that Cu was not analyzed because its concentration in the crust was too low (Glasby and Schulz 1999). In all, 184 point analyses were made at intervals 0.002-0.966 mm (average 0.20 mm) along a vertical transect through the crust but three analyses were omitted because of incomplete datasets. The total analyses of the samples did not add up to 100% because the surface of the polished section was not perfectly smooth and a percentage of the incoming electron beam would not have been reflected normally to the receiver. Apart from the surface sample where the total element analysis summed to only 51.6%, all the other analyses summed from 74.7% to 94.0%. In order to normalize the data for statistical analysis, the analyses were recalculated so that the total analysis summed to 100%. Using these normalized data, it became possible to calculate a correlation matrix. For a correlation matrix of this size, correlation coefficients >0.15 are statistically significant at the 95% confidence level and coefficients >0.22 statistically significant at the 99% confidence level. In order to establish long-term trends in the compositional data, variations in element concentrations with time were fitted by means of polynomial regression. The fifth order fit was seen to give the best approximation to the data.

In addition, 39 bulk samples of CFA-poor material taken from 31 Co-rich Mn crusts dredged from 12 sites (Fig. 2) around Lamont Guyot were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) in order to determine the concentrations of the transition elements (Mn, Fe, Co, Ni and Cu) and rare earth elements (REE) in the crusts. Analytical precision was determined to be $<\pm 6\%$ (relative standard deviation) for the all elements. The analyses were carried out at the Qingdao Institute of Marine Geology.

Dating of the Co-rich Mn crust was carried out using the Co-geochronometer, which is based on the inverse relationship between the Co content of the crusts and their rate of accumulation (Manheim and Lane-Bostwick 1988; Puteanus and Halbach 1988). Based on the analysis of 520 samples of ferromanganese crust from about 250 locations, Puteanus and Halbach (1988) established that the flux of Co into ferromanganese crusts is almost constant over the entire period of growth of the crusts, whereas the flux of Mn into the crusts is inversely proportional to the rate of formation of the crust. It was then possible to derive an

empirical equation relating the growth rate of each layer in a crust to the Co content in that layer by fitting data derived from the ¹⁰Be dating of 20 ferromanganese crusts. This led to the formulation of the equation G (mm Ma⁻¹) = 1.28/ [Co(%)–0.24] where G is the growth rate of the layer of the crust under consideration from which the growth rate and age of individual layers in the crust could be derived without the need for additional radiometric dating. However, modification of this equation is required in cases where phosphatization of the crust has occurred. In this case, no modification was required because of the low P₂O₅ contents of the crust (see previous section).

Frank et al. (1999) confirmed the validity of the Cogeochronometer and showed that it provides detailed information on the growth history of ferromanganese crusts after 10–12 Ma where the ¹⁰Be method cannot be applied. The principal problem with this method is that it does not take into account the occurrence of any hiatuses in growth or erosion of the crust in sections older than 10–12 Ma and can therefore underestimate the age of the crust. However, detailed inspection of the crust failed to reveal any evidence of hiatuses or erosion in this crust (see previous section).

Results

The distribution of the EMPA compositional data with depth through a section of the Co-rich Mn crust from the Lamont Guyot is presented in Table 1 and the correlation matrix calculated from these data is presented in Table 2. The correlation matrix reveals the presence of four principal groups of elements: Mn–Ni–K–Mg–Ca, Co, Fe–P and Si–Al–Fe. In addition, Mn and its associated elements show a significant negative correlation with Fe–P–Si–Al. The patterns of element association are broadly similar to those reported by Wen et al. (1997) and Koschinsky and Hein (2003) for ferromanganese crusts.

In this crust, Fe is present dominantly as Fe oxyhydroxides with only minor amounts of Fe derived from detrital silicates and Fe phosphate. The low content of P_2O_5 in these samples precludes the presence of CFA. If the Si/Al ratio in pelagic clays is taken to be 2.97 (Wen et al. 1997), then it can be calculated that the upper interval of the crust contains on average about 3.5% biogenic siliceous tests (or inorganic opal formed by reprecipitation of dissolved silica derived from dissolution of these tests) and the second interval about 1.6% biogenic silica, as previously reported in Co-rich crusts by Jeong et al. (2000). The biogenic silica content of the lowermost intervals was negligible.

In order to simplify interpretation of the data, the distributions of elements in each of these groups with depth in the crust were plotted and their profiles presented in Fig. 4. Plots of the distributions of Mg, S, Cl, Ti, Cr and O were not considered sufficiently informative to warrant inclusion. It will be noted that Fe is included in two groups, Fe– P and Si–Al–Fe, and that Co is not significantly correlated with any element.

Considering the distribution of element concentrations with depth in the crust, two types of variation can be observed; long-term trends and short-term erratic variations. As shown in Fig. 4, long-term trends in the compositional data are difficult to discern because they are overprinted by short-term erratic variations in composition. Mn, for example, shows an increase in concentration in the crust from 23.3 Ma to 20.4 Ma followed by a steady decline in concentration to the Present, whereas Fe and Si show the opposite trend. Co, on the other hand, appears to have attained its modern concentration at about 22.4 Ma. Average concentrations of the elements in each of the intervals similarly show no systematic changes with time (Table 3).

Plots of the element concentrations were fitted using the fifth order polynomial (Fig. 4). This gives a much clearer picture of long-term trends in element concentrations. These plots show that the data can be divided into three groups. Mn-Ni, Fe-P-Si and Co. In these plots, K, Mg and Ca show only weak associations with Mn, while Al only has a weak association with Fe, suggesting that these associations are not highly significant. Of those elements displaying well-defined trends, Mn and Ni increase in concentration from 23.3 Ma to a maximum at about 20 Ma and then decline steadily to the Present, whereas Fe, P and Si show the opposite trend. Fe displays a minimum value at about 20 Ma and a maximum at about 7 Ma. P and Si show a similar trend, but not as pronounced as for Fe. By contrast, Co displays a double-humped pattern with maxima at about 19 Ma and 4 Ma and minima at 23.3 Ma, about 11 Ma and at the Present. The curve of Mn crustal growth rate is, of course, antipathetic to that of Co because the growth rate of each layer was calculated from the Co content of that layer. Because of its potential importance as an economically valuable element, the minimum and maximum values for Co in the section are listed here (see Table 1): 0.25% at 23.3 Ma, 1.67% at 20.1 Ma, 0.33% at 13.0 Ma, 1.77% at 5.1 Ma and 0.70% at the Present.

Growth rates of the crust calculated for the four intervals from the uppermost to the lowermost based on the agedepth relations in the crust are as follows: 1.3, 1.7, 1.4 and 4.2 mm m.y.⁻¹. The average growth rate for the entire section was 1.6 mm m.y.⁻¹. These growth rates are typical of the very low growth rates (1.7–3.5 mm m.y.⁻¹) for the Co-rich Mn crust 72 DK reported by Puteanus and Halbach (1988) and demonstrate that variations in growth rate have played only a minor role in determining the composition of the crust. The anomalously high rate calculated for the lowermost interval of the crust may be an artefact resulting

 Table 1 Distribution of the EMPA compositional data with depth through the section of the Co-rich Mn crust from the Lamont Guyot

Sample No.	0	Na	Mg	Al	Si	Р	S	Cl	Κ	Ca	Ti	Cr	Mn	Fe	Co	Ni	Н	Age (Ma)
Interval 1 (0-	-7.6 Ma	ı)																
C1	40.47	1.98	1.92	0.62	3.91	0.85	0.45	0.35	0.33	3.02	1.22	1.01	26.22	15.84	0.70	0.25	0.87	0.2
C2	39.83	2.66	1.90	0.67	2.93	0.50	0.55	0.74	0.64	2.69	1.15	0.37	27.46	15.01	1.15	0.83	0.92	0.5
C3	42.04	2.40	1.42	0.52	2.70	0.44	0.69	0.19	0.48	2.74	1.22	0.51	27.13	14.67	1.19	0.36	1.31	0.5
C4	42.80	2.03	1.52	0.47	2.29	0.40	0.52	0.52	0.39	2.72	1.13	0.23	27.98	13.92	0.84	0.71	1.53	0.6
C5	40.00	1.96	1.49	0.78	3.23	0.43	0.48	0.74	0.64	2.81	1.10	0.33	27.43	15.91	1.26	0.47	0.94	0.8
C6	39.31	2.05	1.49	0.51	3.24	0.41	0.50	0.90	0.65	2.71	1.17	0.72	27.11	16.95	1.37	0.07	0.83	1.0
C7	38.66	2.40	1.46	0.42	2.71	0.26	0.93	0.84	0.46	2.60	1.25	0.65	28.53	16.65	1.05	0.44	0.68	1.1
C8	39.05	2.05	1.45	0.59	2.99	0.35	0.65	0.65	0.62	2.87	1.26	0.93	27.37	16.45	1.34	0.63	0.77	1.3
C9	39.99	1.68	1.53	0.47	2.68	0.53	0.55	0.65	0.53	2.83	1.10	0.55	28.04	16.86	0.72	0.36	0.94	1.3
C10	40.57	1.75	1.61	0.45	2.79	0.49	0.38	0.69	0.43	2.65	1.03	0.55	27.55	16.47	0.93	0.55	1.09	1.3
C11	40.13	1.83	1.34	0.55	2.82	0.29	0.52	0.49	0.45	2.77	1.10	0.59	27.42	17.19	0.80	0.72	1.00	1.4
C12	40.06	2.06	1.42	0.77	3.74	0.60	0.48	0.44	0.55	2.63	1.06	0.54	26.09	16.98	1.30	0.40	0.88	1.5
C13	39.55	2.13	1.57	0.66	3.83	0.49	0.39	0.50	0.27	2.47	1.28	0.61	24.47	19.25	1.08	0.63	0.83	1.6
C14	36.86	1.89	1.32	0.55	3.90	0.52	0.91	0.31	0.34	2.75	1.29	1.14	26.59	19.57	1.43	0.46	0.19	1.7
C15	38.25	1.45	1.46	0.57	3.37	0.47	0.38	0.25	0.42	2.58	1.16	1.37	27.61	18.20	1.39	0.53	0.55	1.8
C16	40.87	1.72	1.51	0.34	2.44	0.47	0.52	0.52	0.35	2.87	1.09	0.55	28.03	16.11	1.08	0.38	1.14	2.0
C17	39.03	1.72	1.39	0.31	2.60	0.42	0.61	0.56	0.67	2.77	1.34	0.64	28.31	16.71	1.30	0.83	0.79	2.3
C18	38.62	1.67	1.40	0.53	2.73	0.50	0.49	0.58	0.50	2.48	1.36	0.73	28.03	17.83	1.54	0.32	0.69	2.6
C19	38.48	2.08	1.40	0.45	2.59	0.57	0.60	0.62	0.47	2.64	1.20	0.87	28.37	17.35	1.30	0.34	0.66	2.7
C20	38.81	1.86	1.36	0.53	2.82	0.51	0.43	0.70	0.43	2.44	1.20	0.77	28.63	17.65	0.79	0.36	0.71	2.8
C21	39.85	1.87	1.37	0.46	2.89	0.66	0.62	0.73	0.51	2.60	1.21	0.40	26.54	17.44	1.21	0.71	0.93	2.7
C22	38.60	1.89	1.42	0.51	2.70	0.42	0.43	0.70	0.46	2.70	1.35	1.24	28.15	16.92	1.40	0.40	0.71	2.7
C23	37.45	2.05	1.47	0.54	3.55	0.62	0.78	0.39	0.42	2.40	1.61	1.23	25.73	19.90	1.31	0.20	0.34	2.9
C24	37.52	1.28	1.30	0.49	2.63	0.44	0.30	0.29	0.27	2.42	1.11	0.73	30.01	18.30	1.76	0.68	0.47	3.3
C25	37.03	1.85	1.36	0.57	3.12	0.52	0.57	0.66	0.43	2.43	1.01	1.04	28.05	19.32	1.19	0.51	0.34	3.4
C26	39.66	1.59	1.35	0.38	2.51	0.61	0.39	0.88	0.51	2.61	1.13	0.62	27.98	17.36	0.89	0.60	0.95	3.5
C27	38.89	1.69	1.23	0.48	4.14	0.63	0.38	0.86	0.43	2.49	1.05	0.71	22.96	22.70	0.53	0.10	0.72	3.4
3.5 Ma (close	ing of P	anama	Isthm	us)														
C28	38.92	1.38	1.27	0.47	3.93	0.64	0.35	0.86	0.38	2.44	0.95	0.75	24.04	21.76	0.59	0.53	0.74	3.5
C29	38.45	1.92	1.44	0.24	2.13	0.47	0.47	0.59	0.45	2.97	1.05	0.82	29.48	16.82	1.32	0.68	0.72	3.8
C30	38.39	1.71	1.23	0.51	2.72	0.40	0.39	0.37	0.32	2.62	1.03	1.13	28.58	18.80	0.98	0.19	0.64	4.0
C31	37.87	1.48	1.40	0.29	2.46	0.54	0.72	0.64	0.43	2.68	1.24	0.32	30.43	17.13	1.50	0.36	0.51	4.3
C32	39.48	1.38	1.47	0.39	2.61	0.49	0.56	0.60	0.33	2.53	1.25	1.00	27.52	18.42	0.84	0.29	0.85	4.4
C33	36.13	1.84	1.15	0.48	3.71	0.73	0.72	0.42	0.46	2.65	1.25	1.47	25.53	22.09	1.13	0.14	0.10	4.4
C34	36.66	1.65	1.04	0.55	4.51	0.66	0.29	0.81	0.38	2.32	1.02	0.55	23.99	23.90	1.03	0.40	0.27	4.4
C35	38.47	1.46	1.16	0.53	4.27	0.67	0.34	0.78	0.41	2.25	1.02	0.61	22.58	23.75	0.67	0.38	0.64	4.4
C36	37.87	1.53	1.02	0.57	4.63	0.63	0.26	0.83	0.28	2.39	1.28	0.62	21.46	25.24	0.87	0.00	0.52	4.5
C37	37.87	1.74	1.38	0.51	2.88	0.55	0.46	0.70	0.34	2.53	1.46	1.30	27.65	18.08	1.47	0.54	0.54	4.8
C38	37.67	1.93	1.27	0.47	2.46	0.48	0.55	0.64	0.63	2.28	1.21	1.05	28.75	18.16	1.77	0.15	0.54	5.1
C39	38.42	1.40	1.46	0.47	2.59	0.60	0.44	0.99	0.39	2.54	1.11	0.44	28.06	18.69	1.36	0.37	0.69	5.4
C40	37.60	1.52	1.52	0.60	3.76	0.46	0.28	0.83	0.40	2.51	1.61	0.34	25.84	20.27	1.61	0.37	0.48	5.7
C41	39.26	1.58	1.42	0.45	2.41	0.52	0.38	0.91	0.49	2.54	1.04	0.47	28.60	17.12	1.24	0.69	0.89	6.0
6.2 Ma (incre	ease in (ocean ł	oottom	circula	ation ra	te)												
C42	37.35	1.56	1.52	0.46	2.67	0.40	0.49	0.98	0.53	2.80	1.12	0.51	29.20	17.89	1.12	0.92	0.49	6.3
C43	38.36	1.36	1.43	0.44	2.50	0.36	0.31	0.92	0.47	2.63	1.04	0.54	29.60	17.62	1.15	0.55	0.71	6.6
C44	39.68	1.38	1.23	0.38	2.27	0.56	0.53	1.11	0.43	2.69	1.06	0.26	28.28	17.78	0.93	0.44	0.97	6.7
C45	35.18	1.87	1.27	0.53	4.34	0.74	0.39	1.11	0.28	2.46	1.36	1.09	23.50	24.82	0.60	0.49	-0.01	6.8

Sample No.	0	Na	Mg	Al	Si	Р	S	Cl	Κ	Ca	Ti	Cr	Mn	Fe	Co	Ni	Η	Age (Ma)
C46	37.45	1.52	1.30	0.51	3.95	0.65	0.40	1.05	0.44	2.31	1.16	0.69	24.83	22.41	0.82	0.08	0.44	6.9
C47	36.80	1.72	1.50	0.45	2.89	0.60	0.50	0.73	0.53	2.45	1.03	2.13	28.23	18.54	1.00	0.57	0.32	7.2
C48	37.66	1.88	1.57	0.41	2.56	0.39	0.61	0.67	0.41	2.73	1.37	0.80	29.87	16.63	1.11	0.85	0.49	7.6
Interval 2 (7.	6–18.5	Ma)																
C49	36.65	1.58	1.36	0.41	2.15	0.48	0.49	0.35	0.44	2.52	1.12	0.88	30.93	17.88	1.68	0.75	0.31	8.1
C50	37.49	1.52	1.36	0.36	2.26	0.43	0.41	0.74	0.45	2.79	1.26	1.04	30.13	17.99	1.04	0.23	0.51	8.2
C51	38.56	1.80	1.40	0.33	2.21	0.52	0.43	0.83	0.49	2.68	1.13	0.28	29.49	17.72	0.83	0.54	0.74	8.3
C52	38.20	1.12	1.33	0.53	3.28	0.59	0.24	1.15	0.36	2.45	1.25	0.38	26.14	21.15	0.81	0.37	0.65	8.4
C53	36.34	1.63	1.38	0.65	2.51	0.46	0.53	0.82	0.52	2.74	1.32	1.68	29.78	17.56	1.44	0.40	0.25	8.9
C54	37.85	1.75	1.49	0.32	1.82	0.43	0.38	0.90	0.63	2.73	1.14	0.87	31.33	15.91	1.04	0.77	0.63	9.2
C55	37.92	1.77	1.19	0.28	2.17	0.50	0.34	0.74	0.44	2.58	1.31	0.87	29.97	17.68	1.36	0.25	0.62	9.5
C56	35.47	1.64	1.32	0.49	3.38	0.63	0.45	0.97	0.44	2.76	1.25	0.32	28.79	21.54	0.42	0.12	0.02	9.5
C57	37.51	1.44	1.27	0.43	2.83	0.54	0.38	1.11	0.45	2.62	1.24	0.75	28.37	19.57	0.77	0.21	0.51	9.5
C58	37.18	1.68	1.23	0.59	3.52	0.52	0.26	0.94	0.54	2.45	1.07	0.79	26.31	21.85	0.57	0.07	0.42	9.6
C59	37.49	1.11	1.18	0.46	3.38	0.59	0.32	1.13	0.40	2.45	1.55	0.43	26.62	21.01	1.05	0.36	0.49	9.7
C60	36.41	1.34	1.23	0.59	3.00	0.53	0.38	0.73	0.32	2.69	1.43	0.73	28.22	20.68	0.89	0.59	0.25	9.9
C61	36.91	1.60	1.33	0.48	2.63	0.50	0.43	0.51	0.41	2.53	1.29	3.05	28.59	18.06	0.88	0.45	0.35	10.1
C62	37.41	1.39	1.33	0.39	2.53	0.41	0.35	0.56	0.40	2.52	1.32	0.95	30.18	18.37	1.12	0.29	0.46	10.2
C63	37.19	1.16	1.28	0.46	2.63	0.42	0.48	0.39	0.39	2.72	1.25	0.60	29.74	19.58	0.90	0.43	0.38	10.4
C64	38.35	1.29	1.37	0.32	2.65	0.61	0.34	0.54	0.47	2.59	1.37	0.61	28.48	18.95	0.94	0.48	0.64	10.6
C65	37.41	1.40	1.40	0.48	3.07	0.46	0.32	0.81	0.29	2.73	1.27	1.29	26.89	20.91	0.54	0.24	0.47	10.7
C66	36.20	1.75	1.09	0.41	2.97	0.50	0.32	0.69	0.51	2.66	1.23	1.06	29.37	19.76	0.55	0.70	0.22	10.7
C67	39.20	1.21	1.29	0.49	3.03	0.59	0.37	0.71	0.40	2.68	1.27	0.77	26.97	19.08	0.75	0.39	0.79	10.7
C68	37.12	1.39	1.16	0.57	3.75	0.59	0.25	0.78	0.44	2.70	1.36	0.77	27.02	20.62	0.72	0.40	0.35	10.8
C69	37.53	1.60	1.42	0.36	2.33	0.41	0.27	0.56	0.28	2.63	0.95	1.21	30.12	18.71	0.44	0.68	0.51	10.8
C70	37.74	1.38	1.21	0.48	2.99	0.48	0.39	0.79	0.41	2.77	1.51	0.77	27.39	20.29	0.61	0.27	0.52	10.9
C71	36.73	1.74	1.22	0.44	2.92	0.54	0.66	0.53	0.35	2.69	1.51	1.01	28.80	19.32	0.79	0.49	0.25	11.0
C72	37.84	1.86	1.36	0.30	2.66	0.54	0.49	0.96	0.40	3.00	1.46	0.60	29.19	17.99	0.80	0.00	0.54	11.1
C73	37.27	1.84	1.04	0.37	3.19	0.58	0.25	0.77	0.38	2.61	1.53	1.44	27.26	19.81	0.82	0.40	0.44	11.1
C74	36.45	1.46	1.22	0.41	2.93	0.55	0.39	0.96	0.43	2.86	1.50	0.74	28.83	19.31	0.96	0.71	0.28	11.1
C75	35.04	1.58	1.19	0.44	3.30	0.67	0.38	0.91	0.55	2.92	1.44	1.10	28.27	21.56	0.68	0.04	-0.04	11.2
C76	38.84	1.37	1.44	0.41	2.61	0.55	0.42	1.00	0.45	2.84	1.70	0.17	28.30	18.10	0.94	0.11	0.75	11.3
C77	37.96	1.91	1.31	0.28	2.41	0.42	0.33	0.98	0.51	2.89	1.40	0.69	29.10	18.05	0.91	0.22	0.64	11.3
C78	36.49	1.13	1.37	0.43	2.72	0.52	0.52	0.87	0.44	2.94	1.80	0.49	29.23	19.46	0.88	0.46	0.25	11.3
C79	37.80	1.47	1.27	0.45	2.57	0.55	0.38	0.97	0.42	2.86	1.55	0.77	28.44	18.12	0.70	1.10	0.58	11.3
C80	37.82	1.43	1.29	0.47	2.86	0.55	0.29	1.05	0.47	2.74	1.81	0.31	28.34	18.11	1.33	0.56	0.57	11.4
C81	37.37	1.58	1.17	0.52	2.63	0.44	0.58	0.65	0.36	2.84	1.59	1.02	28.45	18.81	1.12	0.44	0.44	11.5
C82	37.86	1.38	1.36	0.37	2.32	0.47	0.45	0.86	0.41	2.77	1.48	0.55	29.40	18.07	1.14	0.51	0.59	11.7
C83	37.02	1.82	1.20	0.33	2.06	0.47	0.78	0.83	0.37	3.20	1.32	1.19	30.97	16.63	1.05	0.39	0.38	11.8
C84	38.46	1.49	1.52	0.44	2.99	0.41	0.50	0.79	0.43	2.76	1.58	0.66	27.82	18.22	0.55	0.73	0.64	11.8
C85	38.20	1.84	1.33	0.35	1.96	0.50	0.34	0.72	0.49	2.75	1.31	0.75	31.04	16.04	1.22	0.47	0.67	12.0
C86	41.31	1.64	1.38	0.58	3.36	0.49	0.58	0.66	0.51	2.61	1.52	0.93	25.99	15.96	0.88	0.43	1.16	12.4
C87	39.99	1.45	1.39	0.43	2.09	0.40	0.44	0.47	0.52	2.96	1.30	0.44	29.93	15.70	0.98	0.52	0.98	12.8
C88	39.54	1.67	1.48	0.43	2.33	0.41	0.49	1.08	0.40	2.76	1.58	0.43	29.21	16.12	0.80	0.35	0.91	13.0
C90	39.73	1.99	1.32	0.28	1.98	0.41	0.36	1.38	0.44	2.96	1.44	0.46	29.02	16.21	0.43	0.55	1.05	13.0
C91	39.56	2.02	1.28	0.46	2.26	0.39	0.42	1.28	0.50	2.99	1.53	0.23	28.60	16.63	0.33	0.55	0.97	13.0
C92	38.51	2.04	1.35	0.29	1.80	0.25	0.65	1.21	0.47	2.87	1.45	0.81	31.62	14.63	1.14	0.15	0.75	13.2
C93	38.82	2.35	1.48	0.24	1.63	0.39	0.46	1.45	0.51	2.89	1.41	0.38	30.34	15.19	1.00	0.57	0.89	13.2

Table 1 continued

Sample No.	0	Na	Mg	Al	Si	Р	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Н	Age (Ma)
C94	38.86	2.34	1.47	0.32	1.96	0.40	0.60	1.35	0.40	2.85	1.54	0.22	29.83	15.69	0.88	0.47	0.84	13.3
C95	38.91	1.94	1.49	0.35	1.93	0.43	0.48	1.33	0.61	3.00	1.51	0.41	31.22	13.90	1.01	0.64	0.84	13.6
13.7 Ma (Mi	ddle Mi	ocene	climate	e transi	tion)													
C96	39.11	2.17	1.56	0.64	2.05	0.37	0.53	1.12	0.60	3.10	1.28	0.63	30.99	13.00	1.19	0.82	0.85	14.0
C97	38.98	2.21	1.83	0.35	1.20	0.21	0.52	0.94	0.50	2.82	0.99	0.88	34.18	12.04	0.49	0.99	0.84	14.1
C98	38.03	2.29	1.50	0.40	1.73	0.37	0.70	0.92	0.58	3.12	1.42	0.89	30.91	14.89	1.16	0.46	0.63	14.2
14.3 Ma (Mi	ddle Mi	ocene	climate	e transi	tion)													
C99	39.21	2.46	1.54	0.50	1.74	0.31	0.58	1.29	0.69	2.79	1.64	0.78	30.60	13.27	1.15	0.53	0.91	14.3
C100	37.85	2.39	1.49	0.43	2.17	0.38	0.73	0.96	0.51	2.70	1.34	1.10	31.16	14.72	0.80	0.73	0.55	14.3
C102	38.96	1.16	1.38	0.45	2.29	0.32	0.51	0.00	0.22	2.84	1.52	0.74	31.06	16.87	0.68	0.31	0.67	14.5
C103	38.31	1.26	1.04	0.64	3.66	0.57	0.70	0.16	0.44	2.43	1.69	0.79	27.00	20.22	0.62	0.02	0.45	14.5
C104	40.02	1.83	1.34	0.38	2.06	0.37	0.52	0.77	0.38	2.88	1.33	0.47	29.54	16.04	0.86	0.21	1.01	14.5
C105	38.87	1.58	1.50	0.45	2.31	0.48	0.47	0.85	0.38	2.94	1.40	0.34	28.90	16.85	1.30	0.57	0.79	14.6
C106	39.59	1.54	1.56	0.33	2.12	0.40	0.58	0.56	0.29	2.83	1.47	0.81	29.01	15.89	1.31	0.80	0.91	14.7
C107	39.87	1.98	1.22	0.36	1.98	0.34	0.37	1.09	0.50	2.90	1.22	0.74	29.83	14.88	1.21	0.46	1.06	14.8
C108	37.98	1.35	1.59	0.42	2.21	0.45	0.60	0.52	0.36	2.97	1.36	0.81	31.02	16.48	0.91	0.45	0.52	14.9
C109	40.61	2.05	1.48	0.30	0.53	0.32	0.55	1.14	0.50	3.01	1.16	0.68	31.06	13.78	1.13	0.42	1.29	15.1
C110	39.24	2.06	1.46	0.33	1.64	0.34	0.48	1.35	0.58	3.02	1.19	0.65	31.02	14.33	0.90	0.45	0.95	15.2
C111	39.57	2.11	1.66	0.27	1.58	0.26	0.46	1.40	0.53	2.86	1.18	0.26	31.56	13.22	1.14	0.90	1.04	15.3
C112	40.34	2.05	1.41	0.47	2.39	0.36	0.46	1.31	0.55	3.10	1.34	0.95	28.03	15.51	0.41	0.19	1.11	15.3
C113	40.21	1.64	1.15	0.48	2.51	0.38	0.43	0.63	0.42	2.54	1.34	0.53	29.27	16.29	0.80	0.37	1.01	15.3
C114	39.66	1.85	1.05	0.30	1.93	0.48	0.50	0.75	0.42	2.82	1.16	0.72	31.66	14.87	0.63	0.28	0.91	15.4
C115	38.67	1.96	1.29	0.52	2.26	0.45	0.55	0.64	0.43	3.09	1.28	1.71	30.32	15.43	0.64	0.07	0.68	15.4
C116	36.80	2.35	1.29	0.33	1.66	0.15	0.72	0.73	0.58	3 32	1.20	0.41	33.96	14 18	1 15	0.45	0.35	15.5
C117	38.66	1.93	1.65	0.33	1.00	0.42	0.44	0.89	0.50	2.75	1.10	0.50	32.03	13.90	1 47	0.49	0.75	15.5
C118	40.12	2 22	1.05	0.37	1.70	0.42	0.41	0.65	0.30	2.75	1 41	0.32	31.38	13.50	1.47	0.53	1.07	15.5
C119	39.56	2.22	1.22	0.33	1.01	0.38	0.55	0.52	0.45	2.91	1.40	0.29	32.10	13.66	1.25	0.55	0.90	15.0
C120	39.50	1.90	1.22	0.36	1.75	0.38	0.55	0.70	0.52	3.04	1.16	0.53	32.10	12.00	0.87	0.72	0.90	15.7
C121	39.05	2 52	1.45	0.30	1.02	0.21	0.32	1.20	0.52	3.01	1.10	0.33	34.36	10.87	1 1 1	0.91	0.90	15.0
C122	38.83	2.52	1.52	0.26	1.25	0.21	0.55	1.20	0.45	2.08	1.20	0.40	33 31	11.04	1.00	1.07	0.90	16.0
C122	38.89	2.27	1.55	0.20	1.40	0.22	0.55	0.98	0.45	3.04	1.32	0.50	33.66	10.38	1.05	1.07	0.81	16.1
C124	39.46	2.72	1.60	0.40	1 18	0.22	0.59	1.07	0.00	2.85	1.30	0.55	34.28	10.50	1.14	0.76	0.01	16.2
C125	38.27	2.57	1.07	0.40	1.10	0.22	0.53	0.00	0.40	2.05	1.50	0.55	33 34	11 79	1.50	0.70	0.54	16.2
C125	37.86	2.14	1.57	0.31	1.75	0.21	0.55	0.95	0.62	2.96	1.55	0.05	36 31	10.11	1.47	1.03	0.67	16.2
C127	30.50	2.40	1.70	0.38	1.00	0.21	0.32	0.74	0.05	2.90	1.14	0.05	34.65	10.11	1.15	0.89	0.02	16.3
C128	37.35	1.09	1.74	0.30	1.55	0.27	0.87	0.57	0.54	2.90	1.22	2.20	34.15	11.04	1.24	0.85	0.75	16.5
C120	38 30	2.15	1.70	0.35	1.70	0.20	0.86	0.83	0.63	3.36	1.32	1.08	34 50	10.12	1.10	1 1 1	0.41	16.8
C129	38.30	2.15	1.72	0.33	1.17	0.31	0.60	1.25	0.05	2.00	0.07	0.87	35.18	10.12	1.40	0.07	0.00	17.0
C131	38.10	2.42	1.00	0.42	1.56	0.21	0.04	1.20	0.05	2.90	1 1 1	0.57	35.10	0.20	1.09	0.97	0.75	17.0
C122	28.86	2.09	1.79	0.22	1.05	0.23	0.33	1.50	0.00	2.02	1.11	0.52	20.02	14 72	1.04	0.90	0.74	17.4
C133	38.00	2.22	1.37	0.30	1.05	0.41	0.45	1.35	0.44	2.95	1.40	0.10	21.27	14.75	1.20	0.21	0.87	17.0
C134	20.44	2.44	1.35	0.37	1.75	0.45	0.51	1.51	0.39	2.71	1.50	0.15	21.21	14.04	1.01	0.39	0.77	17.0
C135	28.00	2.51	1.37	0.20	1.01	0.27	0.30	1.30	0.50	2.02	1.40	0.34	20.84	14.21	1.25	0.70	0.90	17.7
C130	27.55	2.05	1.27	0.42	1.02	0.40	0.49	1.05	0.51	2.99	1.75	0.54	24.96	14.04	1.00	0.40	0.64	17.9
C137	20 70	2.22 1.94	1.30	0.30	1.20	0.19	0.62	1.43	0.44	5.05 2.17	1.03	0.41	21.04	11.42	1.01	0.17	0.39	10.2
C130	20.25	1.00	1.43	0.40	1.00	0.43	0.51	1.20	0.39	5.17 2.05	1.70	0.77	20.74	14.08	1.37	0.17	0.82	10.4
U139	39.33 05 77 4	1.81 5 M-1	1.1/	0.34	1.90	0.21	0.30	0.92	0.55	2.95	1.0/	0.24	50.70	14.94	1.10	0.39	0.89	10.3
niervai 3 (1)	40.00	, <i>M</i> (<i>a</i>)	1.20	0.42	1.40	0.25	0.42	0.00	0.20	1 00	1 40	0.14	21 (1	12 70	1.00	0.27	1.07	105
C140	40.00	2.18	1.32	0.42	1.46	0.35	0.43	0.98	0.38	2.88	1.42	0.14	31.61	13.78	1.22	0.37	1.07	18.5

Sample No.	0	Na	Mg	Al	Si	Р	S	Cl	Κ	Ca	Ti	Cr	Mn	Fe	Co	Ni	Н	Age (Ma)
C141	38.35	2.15	1.75	0.36	1.05	0.27	0.46	0.91	0.55	2.88	1.23	0.45	36.16	10.63	1.41	0.70	0.71	18.7
C142	38.59	2.47	1.82	0.38	0.79	0.23	0.50	1.14	0.73	2.76	1.15	0.73	36.48	8.97	1.32	1.15	0.81	18.8
C143	40.20	2.03	1.85	0.40	0.95	0.26	0.46	0.79	0.57	2.64	1.11	0.36	37.54	8.18	0.86	0.77	1.02	19.0
C144	40.24	2.03	1.54	0.33	1.30	0.23	0.24	1.23	0.55	3.09	1.17	0.06	34.32	10.17	1.36	0.99	1.16	19.1
C145	39.94	2.44	1.64	0.30	1.03	0.34	0.43	1.20	0.58	2.86	1.18	0.41	34.48	9.33	1.44	1.29	1.09	19.3
C146	40.51	2.28	1.56	0.35	1.16	0.25	0.40	0.73	0.48	2.89	1.19	0.27	34.21	10.30	1.31	0.96	1.15	19.5
C148	40.17	2.22	1.65	0.34	1.26	0.23	0.35	0.99	0.54	2.96	1.27	0.59	34.16	10.46	1.14	0.57	1.10	19.7
C149	39.40	2.03	1.80	0.37	1.01	0.20	0.48	1.01	0.47	2.72	1.08	0.57	35.97	8.99	1.67	1.26	0.94	20.1
C150	39.43	2.27	1.73	0.37	0.99	0.20	0.50	0.89	0.61	2.88	1.06	0.33	35.69	9.78	1.16	1.14	0.94	20.3
C151	38.43	1.63	1.78	0.42	0.90	0.20	0.46	1.33	0.69	2.82	0.98	0.72	37.87	8.66	1.22	1.16	0.75	20.6
C152	40.04	2.57	1.85	0.46	0.76	0.17	0.36	1.37	0.79	2.68	0.94	0.42	36.04	8.54	1.02	0.87	1.13	20.8
C153	39.05	2.26	1.94	0.45	0.88	0.08	0.52	1.29	0.56	2.76	0.99	0.34	37.71	8.54	0.53	1.23	0.86	20.9
C154	39.19	2.11	2.24	0.48	0.87	0.13	0.41	1.07	0.74	2.60	0.90	0.56	37.27	8.19	1.18	1.15	0.89	21.1
C155	39.52	2.14	1.94	0.45	0.92	0.20	0.50	1.01	0.55	2.79	0.88	0.34	35.39	9.78	1.30	1.32	0.98	21.4
C156	38.51	2.49	1.53	0.39	1.31	0.20	0.52	1.57	0.44	3.09	1.15	1.51	33.73	11.02	0.75	0.98	0.82	21.4
C157	36.84	2.51	1.76	0.60	1.43	0.18	1.00	0.81	0.76	3.24	1.11	2.21	34.19	11.13	1.15	0.73	0.34	21.5
C158	36.55	2.67	1.80	0.34	1.19	0.13	1.02	0.79	0.61	3.08	0.99	3.49	33.83	11.25	0.91	1.01	0.32	21.6
C159	40.51	2.21	1.97	0.48	0.91	0.12	0.37	1.35	0.50	2.97	1.10	0.42	35.73	7.81	1.33	1.01	1.20	21.8
C160	39.57	1.71	2.16	0.46	0.99	0.30	0.42	0.86	0.37	2.90	1.14	0.71	35.94	9.53	1.05	0.98	0.92	22.0
C161	36.84	2.51	1.76	0.60	1.43	0.18	1.00	0.81	0.76	3.24	1.11	2.21	34.19	11.13	1.15	0.73	0.34	22.2
C162	38.86	3.02	1.88	0.45	1.08	0.22	0.61	1.43	0.64	3.00	0.87	0.52	35.36	8.58	1.58	1.05	0.87	22.2
C163	41.31	2.53	1.58	0.39	1.15	0.24	0.49	1.47	0.59	2.64	1.20	0.44	32.66	9.68	1.22	1.01	1.39	22.2
C164	40.38	2.91	1.73	0.54	1.05	0.41	0.52	1.84	0.54	2.82	1.05	0.63	33.96	8.67	0.88	0.87	1.19	22.3
C165	40.33	3.02	1.51	0.39	1.32	0.38	0.44	2.64	0.48	3.13	1.17	0.08	30.66	12.07	0.96	0.11	1.31	22.4
C166	39.92	2.78	1.86	0.31	0.93	0.22	0.59	1.88	0.55	3.14	1.19	0.58	33.70	8.95	1.22	1.03	1.15	22.5
Interval 4 (22	2.5–23.3	8 Ma)																
C167	38.09	2.15	1.37	0.53	1.62	0.34	0.49	1.79	0.34	3.28	1.24	0.51	31.04	15.06	0.93	0.47	0.75	22.6
C168	40.02	2.60	1.56	0.50	1.39	0.31	0.44	2.12	0.47	2.89	1.30	0.25	31.28	12.54	0.76	0.40	1.18	22.7
C169	41.61	2.33	1.33	0.46	1.68	0.35	0.39	2.27	0.30	3.05	1.23	0.06	28.42	14.11	0.67	0.21	1.52	22.7
C170	42.18	2.50	1.50	0.44	1.36	0.25	0.50	2.19	0.36	2.86	1.34	0.07	30.04	11.63	0.76	0.41	1.62	22.8
C171	40.47	2.51	1.44	0.33	1.26	0.27	0.59	2.16	0.50	3.09	1.19	0.26	31.38	12.12	0.83	0.33	1.28	22.8
C172	40.81	3.16	1.76	0.40	1.11	0.17	0.38	1.75	0.41	2.93	0.97	0.41	31.92	11.33	0.56	0.58	1.34	22.9
C173	41.00	3.61	1.77	0.29	1.15	0.26	0.75	1.50	0.34	3.17	1.16	0.43	32.04	9.54	0.98	0.71	1.30	22.9
C174	40.92	2.90	1.80	0.50	1.15	0.26	0.69	1.78	0.40	3.18	0.91	0.21	31.96	10.50	0.74	0.77	1.31	22.9
C175	41.92	2.82	1.76	0.30	1.09	0.22	0.53	1.82	0.41	3.05	1.03	0.54	31.91	9.66	0.80	0.59	1.54	22.9
C176	41.82	3.27	1.76	0.39	1.01	0.14	0.43	1.89	0.42	3.05	0.99	0.06	32.48	8.99	0.77	0.96	1.56	23.0
C177	41.81	3.10	1.87	0.42	1.15	0.16	0.45	1.90	0.42	2.97	0.92	0.21	31.32	10.22	0.48	1.02	1.55	23.0
C178	43.34	3.04	1.56	0.37	1.17	0.27	0.36	1.75	0.53	3.00	1.36	0.21	28.75	11.12	0.37	0.94	1.88	23.0
C179	42.94	2.59	1.59	0.38	1.57	0.39	0.48	1.80	0.33	3.06	1.11	0.16	28.91	12.18	0.33	0.47	1.72	23.1
C180	41.22	2.38	1.55	0.43	1.58	0.26	0.65	1.30	0.41	3.26	1.18	0.13	29.53	13.15	0.79	0.84	1.34	23.2
C181	40.97	3.63	1.90	0.43	1.07	0.20	0.75	2.06	0.58	3.05	0.96	0.35	32.33	9.40	0.49	0.47	1.34	23.2
C182	43.45	3.28	1.59	0.41	1.59	0.52	0.50	1.97	0.28	2.95	1.27	0.37	26.75	12.30	0.52	0.39	1.86	23.3
C183	42.07	3.53	1.72	0.40	1.13	0.26	0.51	2.24	0.19	2.95	0.95	0.55	30.05	10.43	0.77	0.59	1.64	23.3
C184	41.55	3.14	3.14	0.30	1.27	0.29	0.70	1.56	0.22	3.14	0.98	1.44	29.91	10.03	0.25	0.68	1.39	23.3

All analyses were recalculated to add to 100% and are expressed in per cent. The analyses were carried out at the Geological Laboratory Center of the China University of Geosciences in Beijing

Table	2 Correl.	ation matrix	calculated	from the H	EMPA com	positional c	lata throug	h the sectic	on of the C	Jo-rich Mn	crust from	the Lamon	t Guyot				
0	1.00																
Na	0.53^{**}	1.00															
Mg	0.41^{**}	0.58^{**}	1.00														
Al	-0.13	-0.21^{**}	-0.14	1.00													
Si	-0.44^{**}	-0.64^{**}	-0.61^{**}	0.55^{**}	1.00												
Ь	-0.38^{**}	-0.61^{**}	-0.59**	0.32^{**}	0.85^{**}	1.00											
S	-0.03	0.36^{**}	0.26^{**}	-0.03	-0.24**	-0.29^{**}	1.00										
ū	0.45^{**}	0.68^{**}	0.35^{**}	-0.29**	-0.55**	-0.44^{**}	-0.05	1.00									
К	-0.06	0.25^{**}	0.26^{**}	-0.02	-0.36^{**}	-0.38^{**}	0.24^{**}	0.08	1.00								
Ca	0.30^{**}	0.54^{**}	0.39^{**}	-0.30^{**}	-0.65^{**}	-0.56^{**}	0.38^{**}	0.46^{**}	0.18^{*}	1.00							
Τi	-0.27^{**}	-0.32^{**}	-0.44**	0.01	0.22^{**}	0.25^{**}	0.01	-0.14	-0.18*	0.04	1.00						
Cr	-0.49^{**}	-0.14	-0.02	0.16^{*}	0.18^{*}	0.10	0.35^{**}	-0.39**	0.08	-0.09	-0.06	1.00					
Mn	0.14	0.45^{**}	0.58^{**}	-0.44^{**}	-0.89**	-0.81^{**}	0.24^{**}	0.30^{**}	0.49^{**}	0.53^{**}	-0.22^{**}	-0.05	1.00				
Fe	-0.55^{**}	-0.73^{**}	-0.74^{**}	0.35^{**}	0.92^{**}	0.85^{**}	-0.30^{**}	-0.51^{**}	-0.43^{**}	-0.63^{**}	0.31^{**}	0.17^{*}	-0.87^{**}	1.00			
Co	-0.20^{**}	-0.07	0.04	-0.01	-0.13	-0.12	0.15^{*}	-0.24**	0.30^{**}	-0.07	0.09	0.01	0.27^{**}	-0.16^{*}	1.00		
ïŻ	0.18^{*}	0.37^{**}	0.59^{**}	-0.23^{**}	-0.59**	-0.61^{**}	0.142	0.18^{*}	0.40^{**}	0.28^{**}	-0.34^{**}	-0.05	0.67^{**}	-0.67^{**}	.022**	1.00	
Н	0.98^{**}	0.62^{**}	0.44^{**}	-0.23^{**}	-0.56^{**}	-0.47^{**}	-0.05	0.59^{**}	-0.02	0.38^{**}	-0.28^{**}	-0.51^{**}	0.23^{**}	-0.63^{**}	-0.19^{**}	0.24^{**}	1.00
	0	Na	Mg	AI	Si	Р	S	CI	K	Ca	Η	Cr	Mn	Fe	Co	Ni	Н
For a signif	correlatio	n matrix bé 99% confi	ised on the	analysis o	f 181 samp	oles, correla	ttion coeffi	cients > 0 .	15 are stat	istically sig	gnificant at	the 95% c	onfidence 1	evel and co	oefficients >	0.22 statist	ically
*Con	elation sig	nificant at t	he 95% cor	nfidence lev	vel; **Corr	elation sign	ificant at t	he 99% coi	nfidence le	vel							

🖄 Springer



Fig. 4 Profiles showing the distributions of 10 elements with depth in the crust based on 181 point analyses by EPMA plus the associated crustal growth rate and Mn/Fe along a vertical transect through the crust (erratic distributions). Because the total analyses of the samples did not add up to 100%, the data were normalized to add up to 100%

in order to facilitate statistical analysis. In order to obtain a clearer picture of the long-term trends in element concentration, profiles of element concentrations were fitted using the fifth order polynomial (smooth curves)

Table 3 Average concentrations of the elements in each of the intervals of the polished section as calculated from the data in Table 1

	Na ₂ O	MgO	Al_2O_3	SiO_2	P_2O_5	SO ₃	Cl	K_2O	CaO	${\rm TiO}_2$	Cr_2O_3	MnO ₂	Fe ₂ O ₃	CoO	NiO
interval 1 (48 samples)	2.40	2.33	0.94	6.60	1.19	1.25	0.67	0.54	3.65	1.98	1.11	42.92	26.32	1.43	0.58
interval 2 (88samples)	2.47	2.31	0.77	4.73	0.96	1.21	0.91	0.56	3.97	2.30	1.07	47.92	23.04	1.25	0.66
interval 3 (27 samples)	3.15	2.90	0.79	2.38	0.52	1.30	1.20	0.68	4.07	1.89	1.04	54.98	14.25	1.48	1.17
interval 4 (18 samples)	3.94	2.86	0.77	2.78	0.63	1.33	1.88	0.46	4.27	1.86	0.51	48.28	16.23	0.83	0.76
total section (181 samples)	2.70	2.46	0.82	4.68	0.92	1.24	0.99	0.56	3.93	2.11	1.02	47.68	21.92	1.29	0.72
Min	1.40	1.69	0.41	1.13	0.18	0.59	0.00	0.23	3.16	1.45	0.08	33.90	11.17	0.32	0.00
Max	4.90	5.21	1.47	9.91	1.95	2.56	2.64	0.94	4.70	3.12	5.09	59.83	36.10	2.25	1.68
Ratio (Max/Min)	3.49	3.07	3.60	8.80	10.59	4.35	~	4.08	1.49	2.16	62.21	1.76	3.23	6.97	~

In this case, element concentrations are calculated for the oxides

from the thinness of this interval and its irregular contact with the underlying substrate.

The transition element contents of the 39 bulk samples of CFA-poor Co-rich Mn crusts taken from around Lamont Guyot were plotted on the triangular diagram of Bonatti et al. (1972) in order to determine the origin of these crusts (cf. Frank et al. 1999). This confirms that these crusts are hydrogenetic in origin (Fig. 5). The North American Shale Composite (NASC)-normalized REE concentrations of these crusts were also plotted using the NASC concentration data of Haskin et al. (1968) to normalize the data (Fig. 6). The crusts are characterized by high Σ REE contents (av. 1889 p.p.m.) and high average Ce/La ratios (4.1) with an average Mn/Fe ratio of 1.3.

Discussion

The compositional variations in the Co-rich Mn crust with time recorded here may be related to a number of factors



Fig. 5 The transition element contents of the bulk samples of the Corich Mn crusts from Lamont Guyot plotted on the triangular diagram of Bonatti et al. (1972)

such as the boundaries between each of the intervals in the crust, the influence of major paleoceanographic events and Milankovitch cycles and the possible inverse correlation between the concentrations of elements associated with the authigenic and detrital phases.

Perhaps the most important of these are the paleoceanographic changes resulting from the opening and closing of oceanic gateways. These are thought to be responsible for large-scale reorganization of global oceanographic circulation and are linked to changes in global climate. The reorganization of global oceanographic circulation can result in variations in the hydrochemical conditions around guyots, which are critical for the deposition of hydrogeneous Fe–Mn crusts on them. The major events occurring in the Pacific since 23 Ma include the Middle Miocene climate transition which occurred between 14.3 Ma and 13.7 Ma (Shevenell et al. 2004) which led to the reestablishment of a major ice sheet on Antarctica by 10 Ma and strengthening of the Antarctic Bottom Water (AABW)



Fig. 6 The North American Shale Composite (NASC)-normalized REE concentrations of the bulk samples of the Co-rich Mn crusts from Lamont Guyot plotted using the NASC concentration data of Haskin et al. (1968) to normalize the data

Flow, an increase in ocean bottom circulation rates at 6.2 Ma and closing the Panama Isthmus at about 3.5 Ma. These events have been documented by Segl et al. (1984, 1989), Zachos et al. (2001) and Frank (2002).

In order to examine the influence of these paleoceanographic events on Mn crustal growth, horizontal lines corresponding to the dates of the boundaries between each of the intervals in the crust at 22.5, 18.3 and 7.5 Ma and to the dates of major paleoceanographic events at 14, 6.2 and 3.5 Ma are plotted on profiles of selected element compositions in the crust (Fig. 3). As is readily apparent, the boundaries between each of these intervals do not coincide with the dates of the paleoceanographic events demonstrating that formation of the intervals was not controlled by these events.

From the fifth order polynomial plots of element concentration shown in Fig. 4, the importance of the negative correlation of Mn and Fe in controlling the long-term compositional trend of the crust and the independent role of Co becomes clear. In principle, these trends may simply reflect an inverse relationship of Mn and Ni to the abundance of Fe oxyhydroxide and detrital silicate minerals in the sample. However, the role of the detrital silicate minerals in this antipathetic relationship is likely to be minor because the EMPA were always made on the columnar zones of the crust and not the intervening areas where the abundance of silicate-rich minerals is much higher.

Of particular importance is the double maximum in the concentration of Co at about 20 Ma and 5 Ma as shown on Fig. 4. This presumably reflects the occurrence of well-developed oxygen minima (accompanied by decreased rates of deposition of Mn and constant rates of scavenging of Co) at these times. Conversely, there has been a triple minimum in the concentration of Co at 23.3 Ma, about 13 Ma and the Present (Fig. 4). These data confirm that by 23.3 Ma the crust had already achieved a content of Co as high as modern concentration (Pulyaeva 1997), but showed no evidence of the abrupt increase in Co concentration and decrease in growth rate at 14 Ma reported by Frank et al. (1999) for the VA 13/2 manganese crust.

From these observations, we conclude that the inverse relationship between Mn and Fe in the crust reflects variations in the influx of Fe of aeolian origin into the Pacific Ocean from the deserts of central Asia (mainly China) with time (Glasby 1991; Bruland et al. 1994; Brutland and Lohan 2004). In the vicinity of the Marcus-Wake Seamount, aeolian deposition appears to be the dominant source of iron to the ocean (Brutland and Lohan 2004). According to Bruland et al. (1994), Fe is introduced into the oceans predominantly in the form of refractory aluminosilicate minerals and converted into the dissolved form within the water column. At the VERTEX site offshore California, for example, 45% of the Fe in deep water (500–

4,000 m) is in the dissolved form. At a water depth of 2,450 m, the concentration of dissolved Fe in seawater formed from particulate Fe is about 22 ng 1^{-1} (Bruland et al. 1994). This Fe would be readily hydrolyzable to form Fe(OH)₃ under seawater conditions (Glasby and Schulz 1999) and is therefore available for adsorption on the surface of the Co-rich Mn crust. These observations are of particular relevance because the Lamont Guyot lies within the region of high atmospheric dust deposition in the central North Pacific where deposition of Fe is dominated by aeolian input (Moore et al. 2002; Bruland and Lohan 2004). However, recent studies have suggested that the solubility of Fe in the dust in seawater is much lower than previously thought (about 2%) (Jickells and Spokes 2001).

On the basis of lead isotope studies, van de Flierdt et al. (2003) concluded that aeolian dust has made only a minimal contribution to the formation of Co-rich Mn crusts since 3.5 Ma. However, the two samples analyzed by these authors were both located in the Pacific Ocean north of 50°N, one off Kamchatka and the other in the Gulf of Alaska, and are located outside the area of maximum input of aeolian dust from Central Asia (Moore et al. 2002). By contrast, Ling et al. (2005) have shown that aeolian transport has been the major factor controlling the Pb isotopic ratios of Co-rich Mn crusts from the western Pacific for the past 40 Ma. In particular, one of these crusts (CLD01) was taken from Lamont Guyot. The results of Ling et al. (2005) therefore strongly support the idea that Fe in Co-rich Mn crust (L09-A-1) was derived mainly from aeolian dust from central Asia.

Halbach and Puteanus (1984) have previously argued that Fe is introduced into Co-rich Mn crusts from the dissolution of calcareous tests. However, Bruland et al. (1994) and Bruland and Lohan (2004) make no mention of the role of calcareous tests in the cycling of Fe in the oceans. Furthermore, Berger (1989) has shown that the Marcus-Wake Seamounts lie within the low productivity zone of the Pacific Ocean and Broecker and Takahashi (1978) that the calcite lysocline is located at a depth of about 3,000 m in the North Pacific Ocean at 20°N. Assuming that the flux of CaCO₃ from the surface waters in the region of the Marcus-Wake Seamounts is <5 g CaCO₃ year⁻¹ (Berger 1989), then the potential amount of Fe in the biogenic calcite available for incorporation in Co-rich Mn crust is 500 p.p.m. (Halbach and Puteanus 1984). With a density of $Fe(OH)_3$ at ~1.3 g cm⁻³, we calculate that the rate of deposition of Fe(OH)₃ on the surface of the crust is about 3.7 mm m.y.⁻¹, which is much higher than the average growth rate of the crust studied here $(1.6 \text{ mm m.y.}^{-1})$. At present, the crust lies above the depth of the calcite lysocline, which means that this Fe is not available for release from the biogenic calcite and incorporation into the Co-rich Mn crust.

However, as shown by van Andel et al. (1975), the dissolution rate of $CaCO_3$ in the ocean was much higher in the Eocene (>38 Ma) and late Miocene-Pliocene (4.5–10.5 Ma) (cf. Halbach and Puteanus 1984) compared to the present. Under these circumstances, Fe would have been incorporated into Co-rich Mn crusts as a result of the dissolution of calcareous tests in addition to the aeolian input. Significantly, the concentration of Fe in the Co-rich crust studied attains its maximum values between about 4.5 Ma and 10.5 Ma, as would be expected on this basis. Figure 7 illustrates this variation of the inferred position of the calcite lysocline with time.

The data presented here show that incorporation of Fe into the Co-rich crust from the Lamont Guyot was at a minimum at about 20 Ma and reached a maximum at about 7 Ma. This leads us to suggest that drying of the Asian mainland by the early Miocene (Guo et al. 2002) led to an increase in aeolian transport of Fe to the oceans. This was supplemented by an additional input of Fe into the crust resulting from the dissolution of CaCO₃ tests between 4.5 Ma and 10.5 Ma. The rate of deposition of Fe into the crust then declined to the Present. The concentrations of other elements, such as Mn, Ni, K, Mg and Ca are antipathetic to Fe. In contrast, Co shows a different trend with two maxima in concentration in the crust at about 20 Ma and 5 Ma.

Milankovitch cycles may also influence the growth of Corich Mn crusts on shorter and longer time scales. These



Fig. 7 Schematic diagram showing variations in the position of the Carbonate Compensation Depth (CCD) (Van Andel et al. 1975; Halbach and Puteanus 1984) and of the inferred position of the calcite lysocline with time assuming a constant depth relationship between the depth of the CCD and that of the calcite lysocline

cycles may be related to orbital precession (23 k.y. and 19 k.y.), obliquity (41 k.y. and 54 k.y.) and eccentricity (95 k.y. and 123 k.y.), as well as highest-order periods of eccentricity at 1.31, 2.04 and 3.47 m.y. (Berger 1977). Milankovitch cycles have already been studied in Co-rich Mn crusts and deep-sea manganese nodules by Hein et al. (1992) and Han et al. (2003). From the vertical profiles of the compositional data presented here, it is clear that our data do not have the resolution to identify Milankovitch cycles <123 k.y. in duration, as reported by Han et al. (2003).

In order to interpret the nature of the short-term erratic variations in element composition with time presented here, the compositional data were subject to spectral analysis using the Statistical Package for the Social Sciences (SPSS) (Fig. 8). The time series of Mn/Fe was interpolated linearly at intervals of 0.01 m.y. The data series was then analyzed using the spectral time series of SPSS and a periodogram obtained. From this, it was possible to identify three periods of 0.61, 0.96 and 1.65 m.y. The second harmonics of these periods are 1.22, 1.92 and 3.30 m.y., respectively, and may correspond to the highestorder periods for eccentricity of 1.31, 2.04 and 3.47 m.y. as reported by Berger (1977). Based on these considerations, it is tentatively suggested that the high frequency oscillations of the Mn/Fe ratios of the Co-rich Mn crust with time may be linked to climatic changes controlled by the highest-order periods of the Milankovitch cycles, as previously proposed by Hein et al. (1992). According to Berger et al. (1992), eccentricity of the Earth's orbit has been almost constant since 500 Ma, which implies that



Fig. 8 Plot of the spectral analysis of the variations of the Mn/Fe ratios of the Co-rich Mn crust with time calculated using the Statistical Package for the Social Science (version 13.0). Three major peaks at 0.61, 0.96 and 1.65 Ma were identified. The peaks at 0.61 Ma and 0.96 Ma are statistically significant at the 95% confidence level and the peak at 1.65 Ma significant at the 90% confidence level. Because of the distance between adjacent data points was in the range 0.01–0.52 Ma with a mean value of 0.16 Ma, it follows that peaks occurring at periods of less than 0.5 Ma are not meaningful

these highest-order periods of eccentricity are applicable for the entire history of Co-rich Mn crust formation.

Migration due to plate motion of the seamounts on which Co-rich Mn crusts form also has the potential to influence their composition. Normally, migration of a seamount can be calculated based on the assumption that the seamount formed at a hot spot and migrated away from that point due to plate motion. However, in the case of the Marcus-Wake and Magellan Seamount clusters, the widespread, apparently random distribution of the volcanoes, recurrent volcanism and lack of anomalous subsidence argue against the influence of any kind of hotspot, linked to a mantle plume (Clouard and Bonneville 2005; Natland and Winterer 2005; Clift 2005). Nonetheless, it is possible to get some idea of the lateral migration of the underlying Pacific Plate by assuming that the plate has been migrating at a rate of 70 mm year⁻¹ in a direction of 290° since 23.3 Ma as has been established for the region of the Ontong Java Plateau (Fig. 4 of Clouard and Bonneville (2005)). This enabled the position of the Lamont Guyot at 23.3 Ma to be estimated to have been at about 16°30' N 174°0' E at 23.3 Ma as shown in Fig. 1. The crust therefore migrated northwards through approximately 5° of latitude during its formation.

Because the Marcus-Wake Seamounts are formed on ocean crust older than 150 Ma (Clouard and Bonneville 2005), the effects of thermal subsidence on Lamont Guyot over the past 23.3 Ma can be discounted (Smith and Sandwell 1997; Clift 2005). The crust would therefore have remained at a water depth close to about 2450 m during its formation. The large discrepancy in age between the crust (23.3 Ma) and the underlying seamount (80.5–90.5 Ma) strongly supports the idea that the crust formed following mass wasting on the slopes of the Lamont Guyot (Jeong et al. 2000). In fact, oceanographic conditions favourable for crust formation began well before 23.3 Ma (Pulyaeva 1997; Frank et al. 1999).

Formation of Co-rich Mn crusts is also strongly influenced by the local oceanic current regime. The ocean bottom current regime in the western Pacific is not well documented. For example, Kawabe et al. (2003) have described the northward transport of ocean bottom water through the Wake Passage and the passages immediately to the west from the SW Pacific, but these flow paths do not extend as far west as the Lamont Guyot at 160°E. The data obtained by these authors suggest that ocean bottom water flow in the western Pacific between the Wake Passage and Mariana Trench is generally rather weak and that thermohaline flow around Lamont Guyot is poorly known. However, internal tides and eddy currents are the dominant form of ocean mixing around seamounts at mid-water depths and are therefore probably more influential to the growth of crusts than thermohaline circulation (Rudnick et al. 2003; Hein 2004; Lavelle et al. 2004). Mikhaĭlik and Khanchuk (2004) have shown that topographic eddies around seamounts can influence the morphology and composition of Co-rich Mn crusts, although the effect on composition may be relatively small (differences of 0.05% and 2.8% in the concentrations of Co and Mn on opposite sides of the seamount, respectively). According to Hein et al. (1993), topographic or dynamic upwelling around seamounts would also bring oxygen from abyssal depths to the sites of crust formation.

However, the most important factors controlling the growth rate and Co content of Co-rich Mn crusts are variations in the intensity and depth of the associated oxygen minimum zone (OMZ) with time. Two hydrographic transects have been undertaken in the vicinity of Lamont Guyot (WOCE P-3 at 28°N and WOCE P-10 at 149°E), which enable these two parameters to be calculated approximately (Schlitzer 2004). These data show that the OMZ at 21°28' N, 159°40' E (corresponding to the location of the crust studied here) occurs at a water depth of about 1,000 m and has a dissolved oxygen content of about 1.1 ml l^{-1} and that the dissolved oxygen content at a water depth of 2,450 m (corresponding to the depth of this crust) is about 2.7 ml l^{-1} , thereby confirming that the crust formed in a well-oxygenated environment beneath a welldeveloped OMZ. The manganese content of seawater, on the other hand, shows the opposite trend.

At the VERTEX site offshore California, for example, the dissolved manganese content of seawater at a water depth of 600 m corresponding to the OMZ was 70 μ g l⁻¹ compared to 40 μ g l⁻¹ at a water depth of 1,900 m (Johnson et al. 1996). This observation supports the view of Halbach and Puteanus (1984) that the OMZ is the main source of Mn for Co-rich Mn crust formation. However, long-term variations in the growth rate and Co content of the crust and the short-term erratic variations in element composition reported here would indicate that there have been major changes in the hydrographic regime around Lamont Guyot since 23.3 Ma.

Frank et al. (1999) have plotted the distributions of selected elements and element ratios with depth in two Corich Mn crusts and one deep-sea Mn crust from the Pacific Ocean, as well as in two crusts each from the Atlantic and Indian Oceans. These data show no consistent trends in the distribution of these elements and element ratios with depth in these crusts even within the same ocean. Profiles of element distributions obtained by other authors similarly show no consistent trends with depth even within the same ocean (Hein et al. 1992; Jeong et al. 2000; this study). However, the residence times for Mn and Fe in the oceans are very short (60 and 500 years, respectively; MBARI 2005) compared to the turnover time of the oceans of about 1500 years (Bender et al. 1977). It is possible therefore that the influence of local variations in the intensity of the OMZ, dissolved oxygen content of the water column, biological productivity of the surface waters and upwelling of deep water around the seamount may be superimposed on each other and be more important than regional factors in accounting for the differences in these profiles. Because the influence of these factors can not easily be disentangled, it follows that our knowledge of the factors controlling the formation of Co-rich Mn crusts may be more rudimentary than we would like to think.

The use of Ce/La ratios in deep-sea manganese nodules as a redox indicator was pioneered by Glasby et al. (1987) and Kunzendorf et al. (1993). In these studies, it was shown that the Ce/La ratios in nodules along a transect from the SW Pacific Basin through the Clarion-Clipperton Fracture Zone to the Peru Basin and thence to the equatorial South Pacific decrease from 9.6 to 1.4, reflecting the decreasing rate of advection of oxygen over the sea floor along the transect. From the data presented here, it can be seen that the average Ce/La ratio of the crusts from the Lamont Guyot (4.1) lies close to the average ratio determined by De Carlo and McMurtry (1992) for Co-rich Mn crusts from the Hawaiian Archipelago and within the range of average ratios of crusts from eight areas in the Pacific (3.7–7.4) reported by Hein et al. (2000). These results confirm that formation of these crusts was associated with well-oxygenated conditions.

Plots of the NASC-normalized REE concentrations of these crusts are unusual in showing positive Gd and Ho anomalies (Fig. 6). A positive Gd anomaly in Co-rich Mn crusts was first reported in Co-rich Mn crusts from the Marshall Islands by Hein et al. (1988) but did not receive any further attention. However, it is possible that the positive anomalies for Gd and Ho observed in Fig. 6 are a consequence of the lanthanide tetrad effect described by Bau (1999) and Ohta and Kawabe (2001). In order to test this hypothesis, the significance of the third tetrad Gd-Tb-Dy-Ho and fourth tetrad Er-Tm-Yb-Lu were quantified using the procedure described by Monecke et al. (2002). The results show that the third tetrad was significant but the fourth tetrad was not. These calculations enable us to discount the influence of the lanthanide tetrad effect on the REE distribution in these crusts.

From the preceding discussion, it is clear that a number of diverse factors influence the formation of Co-rich Mn crusts. Figure 9 shows a summary of the relative importance of some of the more important of these factors. We concur with Halbach and Puteanus (1984) that environ-

Fig. 9 Schematic

representation of some of the major processes controlling the growth of a Co-rich Mn crust in the Marcus-Wake Seamount cluster



mental factors such as biogenic productivity, range and depth of the lysocline and calcium carbonate compensation depth, rate of carbonate dissolution and activity of AABW are all important in controlling the growth of Co-rich Mn crusts, but are unable to assess the relative importance of these factors based on this detailed study of a single crust.

Conclusions

A detailed study of a Co-rich Mn crust from the Lamont Guyot in the Marcus-Wake Seamount cluster shows that the crust began forming at 23.3 Ma following mass wasting on the slopes of the guyot. The average growth rate for the entire section of the crust was 1.6 mm m.y.⁻¹. The crust migrated northwards through about 5° of latitude since its formation at 23.3 Ma. It is presently located in a well-oxygenated environment beneath a well-developed OMZ.

In section, the crust was divided into four intervals based on textural characteristics of the crust. However, the boundaries between these intervals do not appear to show any relationship to major paleoceanographic events in the world ocean.

Long-term and short-term trends in element composition have been determined within the crust. Long-term trends are probably the result of variations in the aeolian transport of Fe into the western Pacific from Asia, which reached a maximum at about 7 Ma together with additional inputs of Fe to the crust from the dissolution of calcareous tests between about 10.5 Ma and 4.5 Ma. Astronomical forcing may have been, in part, responsible for the short-term erratic variations in the composition of the crust. A schematic representation of the relative influence of geological, oceanographic and astronomical processes on the formation of the crust has been presented.

Plots of NASC-normalized REE concentrations of bulk samples of Co-rich Mn crusts from the Lamont Guyot are unusual in showing positive Gd and Ho anomalies. However, these observations are not consistent with the influence of the lanthanide tetrad effect in these crusts.

Acknowledgements We would like to thank Professor K.S. Johnson (Monterey Bay Aquarium Research Institute) for helpful advice. Our work was sponsored by projects DY 105-01-04-02 and DY 105-01-04) from the China Ocean Mineral Resources R&D Association (COMRA), the project (Grant No. 40376016) of the National Natural Science Foundation of China and project (2006DFB21620) from the Ministry of Schience and technology of P. R. China. The cruise of R/V Dayang Yihao was organized by COMRA.

References

181

oxidation, Y-Ho fractionation, and lanthanide tetrad effect. Geochim Cosmochim Acta 63:67–77

- Bender ML, Klinkhammer GP, Spencer DW (1997) Manganese in seawater and the marine manganese balance. Deep-Sea Res 24:799–812
- Berger A, Loutre MF, Laskar J (1992) Stability of the astronomical frequencies over the Earth's history for paleoclimate studies. Science 255:560–566
- Berger AL (1977) Support for the astronomical theory of climatic change. Nature 269:44–45
- Berger WH (1989) Global maps of ocean productivity. In: Berger WH, Smetacek VS, Wefer G (eds) Productivity of the oceans: present and past. Wiley & Sons, NY, pp 429–455
- Bonatti E, Kraemer T, Rydell HS (1972) Classification and genesis of iron-manganese deposits, In: Horn DR (ed) Ferromanganese deposits on the ocean floor. National Science Foundation, NY, pp 149–166
- Broecker WS, Takahashi T (1978) The relationship between lysocline depth and *in situ* carbonate ion concentration. Deep-Sea Res 25:65–95
- Bruland KW, Lohan MC (2004) Controls of trace metals in seawater. In: Elderfield H (ed) Treatise on geochemistry volume 6 the oceans and marine geochemistry. Elsevier, Amsterdam, pp 22– 47
- Bruland KW, Orians KJ, Cowen JP (1994) Reactive trace metals in the stratified central North Pacific. Geochim Cosmochim Acta 58:3171–3182
- Clift P (2005) Sedimentary evidence for moderate mantle temperature anomalies associated with hotspot volcanism. In: Foulger GR, Natland JH, Presnall D, Anderson DL (eds) Plates, Plumes and Paradigms. Geol. Soc. Am. Spec. Pap. 388:279–287
- Clouard V, Bonneville A (2000) Ages of seamounts, islands and plateaus on the Pacific Plate. University of French Polynesia, Tahiti, pp 42
- Clouard V. and Bonneville A. (2005) Ages of seamounts, islands and plateaus on the Pacific Plate. In: Foulger GR, Natland JH, Presnall D, Anderson DL (eds) Plates, Plumes and Paradigms, Geol. Soc. Am. Spec. Pap. 388:71–90
- De Carlo EH, McMurtry GM (1992) Rare-earth element geochemistry of ferromanganese crusts from the Hawaiian Archipelago, central Pacific. Chem Geol 95:235–250
- Frank M O'Nions RK, Hein JR, Banakar VK (1999) 60 Myr records of major elements and Pb-Nd isotopes from hydrogenous ferromanganese crusts: Reconstruction of seawater paleochemistry. Geochim Cosmochim Acta 63:1689–1708
- Frank M (2002) Radiogenic isotopes: tracers of past ocean circulation and erosional input. Rev Geophys 40(1), Article number 1001
- Glasby GP (1991) Mineralogy, geochemistry, and origin of Pacific red clays: a review, NZ J Geol Geophys 34:167–176
- Glasby GP, Gwozdz R, Kunzendorf H, Friedrich G, Thijssen T (1987) The distribution of rare earth and minor elements in manganese nodules and sediments from the equatorial and S.W. Pacific, Lithos 20:97–113
- Glasby GP, Schulz HD (1999) E_H , pH diagrams for Mn, Fe, Co, Ni, Cu and As under seawater conditions: application of two new types of E_H , pH diagrams to the study of specific problems in marine geochemistry. Aquat Geochem 5:227–248
- Guo ZT, Ruddiman WF, Hao QZ, Wu HB, Qiao YS, Zhu RX, Peng SZ, Wei JJ, Yuan BY, Liu TS (2002) Onset of Asian desertification by 22 Myr ago inferred from loess deposits in China. Nature 416:159–163
- Halbach P, Puteanus D (1984) The influence of the carbonate dissolution rate on the growth and composition of Co-rich ferromanganese crusts from Central Pacific seamount areas. Earth Planet Sci Lett 68:73–87
- Bau M (1999) Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: experimental evidence for Ce

- Han X, Jin X, Yang S, Fietzke J, Eisenhauer A (2003) Rhythmic growth of Pacific ferromanganese nodules and their Milankovitch climatic origin. Earth Planet Sci Lett 211:143–157
- Haskin LA, Haskin MA, Frey FA, Wildeman TR (1968) Relative and absolute terrestrial abundances of the rare earths. In: Ahrens LH (ed) Origin and distribution of the elements, 1. Pergamon Press, Oxford, pp 889–911
- Hein JR (2004) Cobalt-rich ferromanganese crusts: global distribution, composition, origin and research activities, in: Minerals other than polymetallic nodules of the international seabed area. Proceedings of a workshop held on 26–30 June 2000 in Kingston, vol 1, Jamaica, pp 188–272
- Hein JR, Schwab WC, Davis AS (1998) Cobalt- and platinum-rich ferromanganese crusts and associated substrate rocks from the Marshall Islands. Mar Geol 78:255–283
- Hein JR, Bohrson WA, Schulz MS, Noble M, Clague DA (1992) Variations in fine-scale composition of a central Pacific ferromanganese crust: Paleoceanographic implications. Paleoceanogr 7:63–77
- Hein JR, Yeh H-W, Gunn SH, Sliter WV, Benninger LM, Wang C-H (1993) Two major episodes of Cenozoic phosphogenesis recorded in equatorial Pacific seamount deposits. Paleoceanography 8:293–311
- Hein JR, Koschinsky A, Bau M, Manheim FT, Kang J-K, Roberts L (2000) Cobalt-rich ferromanganese crusts in the Pacific. In: Cronan DS (ed) Handbook of marine mineral deposits. CRC Press, Boca Raton, pp 239–279
- Jeong KS, Jung HS, Kang JK, Morgan CL, Hein JR (2000) Formation of ferromanganese crusts on northwest intertropical Pacific seamounts: scanning electron photomicrography and microprobe chemistry. Mar Geol 162:541–559
- Jickells T, Spokes L (2001) Atmospheric inputs to the oceans. In Turner D, Hunter K (eds) Biogeochemistry of seawater. Wiley, NY, pp 85–121
- Johnson KS, Coale KH, Berelson WM, Gordon RM (1996) On the formation of the manganese maximum in the oxygen minimum. Geochim Cosmochim Acta 60:1291–1299
- Kawabe M, Fujio S, Yanagimoto D (2003) Deep-water circulation at low latitudes in the western North Pacific Ocean. Deep-Sea Res I 50:631–656
- Koschinsky A, Hein JR (2003) Uptake of elements from seawater by ferromanganese crusts: solid-phase associations and seawater speciation. Mar Geol 198:331–351
- Kunzendorf H, Glasby GP, Stoffers P, Plüger WL (1993) The distribution of rare earth and minor elements in manganese nodules, micronodules and sediments along an East-West transect in the South Pacific. Lithos 30:45–56
- Lavelle JW, Lozovatsky ID, Smith DC (2004) Tidally induced turbulent mixing at Irving Seamount–Modeling and measurements. Geophys Res Letts 31:L10308
- Ling H-F, Jiang S-Y, Frank M, Zhou H-Y, Zhou F, Lu Z-L, Chen X-M, Jiang Y-H, Ge C-D (2005) Differing controls over Cenozoic Pb and Nd isotope evolution of deepwater in the central North Pacific. Earth Planet Sci Lett 232:345–361
- Manheim FT, Lane-Bostwick CM (1998) Cobalt in ferromanganese crusts as a monitor of hydrothermal discharge on the Pacific sea floor. Nature 335:59–62
- Melnikov ME, Pulyaeva IA (1995) Ferromanganese crust deposits on Marcus-Wake and Magellan Seamounts, western Pacific: structure, composition and age. Geol Pacif Ocean 11:525–540

- Mikhaĭlik EV, Khanchuk AI (2004) Role of Taylor-Hogg topographic vortices in the formation of cobalt-manganese crusts on guyots of the Magellan Seamounts, Pacific Ocean. Trans (Dokl) Russian Acad Sci/Earth Sci Sect 394(1):19–21
- Monecke T, Kempe U, Monecke J, Sala M, Wolf D (2002) Tetrad effect in rare earth element distribution patterns: a method with application to rock and mineral samples from granite-related rare earth deposits. Geochim Cosmochim Acta 66:1185–1196
- Moore JK, Doney SC, Glover DM, Fung IY (2002) Iron cycling and nutrient limitation patterns in surface waters of the World Ocean. Deep-Sea Res II 49:463–507
- Natland JH, Winterer EL (2005) Fissure control on volcanic action in the Pacific. In: Foulger GR, Natland JH, Presnall D, Anderson DL (eds), Plates, Plumes and Paradigms, Geol. Soc. Am. Spec. Pap. 388:687–710
- Nealson KH (1997) Nannobacteria-size limits and evidence. Science 276:1776
- Ohta A, Kawabe I (2001) REE(III) adsorption onto Mn dioxide (δ -MnO₂) and Fe-oxyhydroxide: Ce(III) oxidation by δ -MnO₂. Geochim Cosmochim Acta 65:695–703
- Pulyaeva I. (1997) Stratification of ferromanganese crusts on the Magellan seamounts. Proc 30th Int'l Geol Congr 13:111–128
- Puteanus D, Halbach P (1998) Correlation of Co concentration and growth rate – A method for age determination of ferromanganese crusts. Chem Geol 69:73–85
- Rudnick DL, Boyd TJ, Brainard RE, Carter GS, Egbert GD, Gregg MC, Holloway PE, Klymak JM, Kunze E, Lee CM, Levine MD, Luther DS, Martin JP, Merrifield MA, Moum JN, Nash JD, Pinkel R, Rainville L, Sanford TB (2003) From tides to mixing along the Hawaiian Ridge. Science 301:355–357
- Schlitzer R. (2004) Ocean Data View (http://www.awi-bremerhaven.de/ GEO/eWOCE/)
- Segl M, Mangini A, Beer J, Bonani G, Suter M, Wölfi W (1989) Growth rate variations of manganese nodules and crusts induced by paleoceanographic events. Paleoceanography 4:511–543
- Segl M, Mangini A, Bonani G, Hofmann HJ, Nessi M, Suter M, Wölfi W, Friedrich G, Plüger WL, Wiechowski A, Beer J (1984) ¹⁰Bedating of a manganese crust from the central north Pacific Ocean and implications for ocean palaeocirculation. Nature 309:540– 543
- Shevenell AE, Kennett JP, Lea DW (2004) Middle Miocene Southern Ocean cooling and Antarctic cryosphere expansion. Science 305:1766–1770
- Smith WHF, Sandwell DT (1997) Global sea floor topography from satellite altimetry and ship depth soundings. Science 277:1956– 1961
- Van Andel TjH, Heath GR, Moore TC (1975) Cenozoic history and paleoceanography of the equatorial Pacific Ocean. Mem Geol Soc Am 143:1–134
- van de Flierdt T, Frank M, Halliday AN, Hein JR, Hattendorf B, Günther D, Kubik PW (2003) Lead isotopes in North Pacific deep-water implications for past changes in input sources and circulation patterns. Earth Planet Sci Lett 209:149–164
- Wen X, De Carlo EH, Li YH (1997) Interelement relationships in ferromanganese crusts from the central Pacific Ocean: the implications for crust genesis. Mar Geol 136:277–297
- Zachos J, Pagani M, Sloan L, Thomas E, Billups K (2001) Trends, rhythms, and aberrations in global climate 65 Ma to Present. Science 292:686–693