Full length Article

Composition and genesis of ferromanganese deposits from the northern South China Sea

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ARTICLE INFO

Article history:

Received 4 November 2016

Received in revised form 6 February 2017

Accepted 6 February 2017

Available online 9 February 2017

Keywords:

Fe–Mn deposits

Genetic model

Rare earth elements

Hydrogenetic–diagenetic growth

Hydrocarbon seeps

Northern South China Sea

ABSTRACT

Marine ferromanganese (Fe–Mn) nodules and crusts are archives of past environmental conditions and potential mineral resources. Over the last 30 years, many have been discovered in the northern South China Sea (SCS). To determine the origin of the Fe–Mn deposits, a comprehensive laboratory analysis of physical properties, mineralogy and geochemistry was conducted on newly collected Fe–Mn nodule/crust samples. The results revealed that there are three types of Fe–Mn deposits: (1) Fe-rich nodules containing essentially goethite occur on the northeastern slope of the SCS, with high Fe, low Mn (Mn/Fe = 0.03) and low trace metals and rare earth elements concentrations; (2) Smooth Fe–Mn nodules and crusts composed of asbolane, todorokite and CFA occur along the northwestern marginal of the SCS that have similar Fe and Mn contents (Mn/Fe = 1.21), moderate trace metal enrichments, and a positive Ce anomaly; (3) Fe–Mn nodules and crusts composed of asbolane, todorokite and birnessite that occur in the central basin of the SCS have higher Mn and lower Fe contents (Mn/Fe = 1.45). This depositional pattern was associated with major changes in oceanographic conditions and tectonic regimes. The northeastern slope deposits occur in a contourite depositional system, are strongly enriched in Fe relative to Mn (average 38.7% and 0.96%, respectively), formed from the combination of hydrogenetic and diagenetic processes. We propose a new genetic model for Fe–Mn nodules, which formed through the oxidation of pyrite and pyrite-barite concretions that formed by rapid early diagenetic growth (average 3320 mm/Myr) on continental margins above the carbonate compensation depth, and dominated by hydrocarbon seep structures and strong erosive action of bottom currents along the northeastern slope. In contrast, the introduction of vigorous deep-water flow from the North Pacific promoted the slow growth (4–7 mm/Myr) of hydrogenetic Fe–Mn nodules and crusts along the northwestern margin. Finally, hydrogenetic growth of Fe–Mn nodules and crusts in the central basin may have been enhanced by volcanic processes. Our data provide new insights into the genesis and province characteristics of the Fe–Mn nodules and crusts of the northern SCS.

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1. Introduction

Ferromanganese (Fe–Mn) deposits are metal-rich chemical sediments that are potential archives for geological and environmental changes and are potential mineral resources (Ling et al., 1997; Ren et al., 2007). They may contain base metals and strategic and

critical elements such as Cu, Ni, Zn, Co, rare earth elements (REEs) and are being considered for future mining (Rona, 2008; Hein et al., 2013). Oceanic Fe–Mn deposits include Fe–Mn crusts, also referred as cobalt-rich crusts, polymetallic nodules, and hydrothermal crusts and impregnations. Numerous reviews of Fe–Mn deposits genetic processes and distributions exist (Halbach et al., 1981; Aplin and Cronan, 1985; Hein et al., 1997, 2000, 2013). These deposits are commonly distinguished as hydrogenetic, diagenetic, mixed hydrogenetic–diagenetic or hydrothermal deposits, and are present in many geological and oceanographic settings (Dymond et al., 1984; Bau et al., 2014; Josso et al., in press). The terminology is based on the type of fluid from which the Fe–Mn oxide precipitate. In general, marine Fe–Mn oxide precipitates are defined as

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purely hydrogenetic when all constituents are derived from cold seawater, as diagenetic when all constituents are derived from cold oxic or suboxic sediment porewaters, and as hydrothermal when they precipitate in the vicinity of vent sites from fluids with temperatures higher than ambient bottom waters (Bau et al., 2014; González et al., 2016). However, in many places, Fe-Mn nodules and crusts form through a combination of fluid sources thereby exhibiting a mixed origin, primarily either hydrogenetic-diagenetic or hydrothermal-hydrogenetic (Hein et al., 1997; Baturin et al., 2014; González et al., 2016).

It is widely accepted that Fe-Mn oxides occur in a wide variety of geological settings (abyssal plains, spreading centers, oceanic highs) and marine environments (deep oceans, continental margins, shallow waters, and epicontinental seas) (Cronan, 1977; Glasby et al., 1997; Verlaan et al., 2004; González et al., 2007). Much of the research on Fe-Mn oxides has focused on open-ocean oxides from areas such as the Clarion-Clipperton Fracture Zone (CCFZ) in the central Pacific Ocean, the Central Indian Ocean Basin and the Peru Basin in the southeastern Pacific Ocean (Rona, 2008; Kuhn et al., 2012). Only a few studies focused solely on continental margin Fe-Mn nodules and crusts, such as from Galicia Bank (NW Atlantic Iberia margin) (González et al., 2016), Gulf of Cadiz (González et al., 2012), California continental-margin (Hein et al., 2005; Conrad et al., in press), Canary Island Seamount Province (Marino et al., in press) and the Philippine Sea (Xu et al., 2006).

The South China Sea (SCS) is one of the largest marginal seas of the western Pacific, it is subject to relatively large terrestrial inputs, metal fluxes from continental shelf and slope hypoxic sediment, seasonal upwelling, high primary productivity, and a well-developed oxygen minimum zone (OMZ) (Xie et al., 2003; Chen and Chen, 2006; Milliman and Farnsworth, 2011; Liu et al., 2015). Because of the enormous amount of terrigenous sediment input into marginal seas, Fe- and Mn-oxide precipitates are easily diluted making it difficult to enrich metals of potential economic interest, and deposits can be buried quickly by sediments (Zhang

et al., 2013). For these reasons, it is well known that the Fe-Mn nodules and crusts of the SCS occur in the central basin, far from the continent and with low sedimentation rates (Wang et al., 1986; Bao and Li, 1993). In recent years, Fe-Mn nodules and crusts were occasionally discovered in areas such as the northeastern or northwestern SCS (Lin et al., 2003; Zhang et al., 2012). Available geochemical data for Fe-Mn nodules and crusts are limited, and basin-wide samples from the northern SCS are lacking, which does not allow for an overall understanding of the mechanisms involved in scavenging of metals from seawater and porewater.

This paper presents detailed physical, textural, mineralogical, and geochemical descriptions of Fe-Mn nodule and crust samples recovered from the northern SCS from 2005 to 2013. Combined with recently available mineralogical and geochemical data of Fe-Mn nodules and crusts throughout the northern SCS, we propose provinces, genetic models, and metal sources of the Fe-Mn nodules and crusts. In addition, we present a comparative analysis with other deep-seabed Fe-Mn deposits, shallow-water and continental margin nodules and crusts from other ocean basins and tectonic settings of the world.

2. Geological and oceanographic framework

The SCS is tectonically situated at the intersections of the Eurasian, Pacific, and Indo-Australian plates and, thus its geology had been greatly affected by these surrounding lithospheric plates (Fig. 1a). It is characterized by conjugate passive continental margins in both the north and south (Sun et al., 2014). Its bottom topography is very complex, widely variable with several plateaus, troughs, valleys and island reefs. The study area (106–122°N and 12–26°E, Fig. 1b) is located in the northern SCS, which has a broad continental shelf (<200 m water depth) and a large deep basin (maximum water depth > 4000 m).

Since the Mesozoic, the northern continental margin of the SCS went through a succession of geotectonic regimes and was strongly dissected by eroded deep-marine channels, submarine canyons,

Fig. 1. (a) Sketch map of the South China Sea and surrounding basins; (b) Overview map of the northern part of South China Sea (SCS), with the locations of subsurface ferromanganese nodule and crust samples in the northern SCS (see Table 1 for GPS locations). Province A = Northeastern SCS (NESCS); Province B = Northwestern SCS (NWSCS); Province C = Central Basin SCS (CBSCS). The purple solid arrows are pathways for the intrusion of the Northern Pacific Deep Water into SCS via the Luzon Strait (Gong et al., 2012; Lüdmann et al., 2005); The pink arrows represent the assumed deep-water current circulation pathways in the northern SCS (Shao et al., 2007; Wang et al., 2010; Zheng and Yan, 2012). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and slope gullies. All of these acted as active conduits for the delivery of clastic sediments from the SCS shelf and upper slope into the deep marine environment (Chiu and Liu, 2008; Gong et al., 2015). Within the study area, the extensional and strike-slip fault system of the Dongsha Islands forms a favorable migration system of fracture conduits or channels through which methane bearing fluids migrate into shallow sediments and vent at the seafloor (Fig. 2a) (Chen et al., 2005). The seafloor seep sites are, in general, characterized by the occurrence of seep carbonates, chemosynthetic benthic communities, tube worms and special topography (such as mud volcanoes, pockmark and mud diapir), which are typical of methane seepage in the modern marine sediments (McDonnell et al., 2000; Ge et al., 2010; Wang et al., 2014).

The central SCS basin is floored primarily by oceanic crust (Taylor and Hayes, 1983; Briais et al., 1993). Cenozoic sedimentary basins controlled by plate motions and tectonic activity, especially by extension and other dynamic events, are roughly parallel to the NE-striking faults (Fig. 2b) (Suo et al., 2014). Structurally and bathymetrically, it is complicated with extinct spreading centers, transform faults, ridges, and late-stage seamount volcanism after the cessation of seafloor spreading (e.g., Yan et al., 2006; Xu et al., 2012). According to its water depth and seafloor topographic features, the SCS basin is confined by the continental-ocean boundary and is subdivided into northwest, east and southwest sub-basins (Barckhausen et al., 2014). Especially, the East sub-basin, the largest basin among the three SCS sub-basins, is characterized by many widely distributed seamounts. Based on a limited amount of age data (Wang et al., 1985; Yan et al., 2014), the seamounts generally show a younger trend from the northwest sub-basin to the Huangyandao seamount chain, approximately corresponding to the age of the underlying oceanic crust (Fig. 2b). The approximately E-W-trending Zhenbei-Huanyan seamounts chain is a post-spreading magmatic chain formed after the cessation of seafloor spreading (Tu et al., 1992; Briais et al., 1993; Wang et al., 2009; Xu et al., 2012). Consequently, the igneous rocks from SCS seamounts and volcanoes in the surrounding areas contain a record of the source and evolution of intraplate or post-spreading volcanism that commenced as early as ~18 Ma and is still active at the northern margin of the SCS and in the Indochina block (Wang et al., 1985).

Modern oceanic circulation in the SCS is influenced mainly by the semi-enclosed-basin physiography, the main oceanic water masses, and atmospheric circulation (Qu et al., 2006b; Zhu et al., 2010). It preserves water exchange through straits with the Pacific

Ocean, Indian Ocean, and the adjacent marginal seas (Fig. 1b). In the East Asia region, differential heating between the NW Pacific and the Asian land-mass leads to a seasonal reversal of monsoon winds and resultant seasonal surface circulation patterns over the SCS (Fang et al., 2012). Summer monsoon winds flow weakly from the southwest towards the northeast and vice versa in winter, leading to anticyclonic and cyclonic basin circulation, respectively (Shaw and Chao, 1994). The local bathymetry and stratification of the water column result in Ekman pumping and transport, which are important in generation of summer upwelling of cold, nutrient-rich and high-salinity water offshore SE Vietnam (Dippner et al., 2007; Chen et al., 2012). The upwelled water is transported off shore and nutrient distributions are affected by mixing, biologic, drawdown, and particulate scavenging (Tang et al., 2004).

The Luzon Strait is the only deep connection between the SCS and the North Pacific, with the deepest sill at about 2400 m, located in the Bashi Channel (Wang and Li, 2009; Li and Gong, 2016). Numerous studies of deep-water circulation in the SCS (i.e., below 2000 m) have been undertaken to constrain the inflow and the pathway of the North Pacific Deep Water (NPDW) into the SCS (Qu et al., 2006b; Tian et al., 2006; Wang et al., 2011; Zhao et al., 2014). The NPDW, characterized by low temperature (1.6 °C) and high salinity (34.62‰), sinks into the deep SCS basin immediately after it crosses the Luzon Strait (Fig. 3) (Wyrski, 1961). The basin-scale oxygen distribution suggests that deep water that enters the SCS is transported north and westward to the northern slope of the SCS and then southward along its western margin (Fig. 1b) (Li and Qu, 2006; Qu et al., 2006a); It enhances vertical mixing and potentially contributes to upper layer circulation (Qu et al., 2006b; Tian et al., 2009). Moreover, a series of NE- and WSW-migrational channels developed on the northern slope (Zhu et al., 2010; He et al., 2013; Li et al., 2013a). Most contourite deposits are linked to bottom water activity, which has paleoceanographic/paleoclimatic implications in this area (Chen et al., 2014; Kuang et al., 2014; Gong et al., 2015).

3. Materials and methods

3.1. Sample collection

As part of the integrated research cruises organized by the South China Sea Institute of Oceanology (SCSIO, Chinese Academy of Sciences) since 2005, 15 Fe-Mn nodule samples were collected

Fig. 2. Bathymetric maps of ferromanganese deposit areas; See location in Table 1 and same legend as Fig. 1b. (a) Bathymetric map of NESCS ferromanganese deposits and seepage associated structure (Tong et al., 2013; Zhang et al., 2015); (b) Bathymetric map of CBSCS ferromanganese deposits (modified from He et al. (2016)). The spreading axes are yellow double lines. The black dashed line marks the Zhongnan Fault Zone. There are three fossil spreading centers: the first one is oriented E-W in the northwest (NW) sub-basin; the second one is oriented E-W in the east sub-basin (near the present 17°N); and the third one is also in the east sub-basin (15.5°N) but extends southwestward into the southwest (SW) sub-basin. Data are from (Briais et al., 1993). The ages of seamounts are from (Yan et al., 2008). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Hydrological setting of ferromanganese deposit area; (a) Salinity-depth section view crossing the NWSCS; (b) Base map with the CTD data distribution of the northern SCS; (c) Temperature-depth section view crossing the study area.

from seven stations in the northern SCS (Table 1, Fig. 1b). Four stations (05E105, 05E204, 10E204B and ZX31) are located in the northeastern South China Sea (NESCS), while two stations (05E107 and 09KJ22) are in the northwestern South China Sea (NWSCS). The final station (J-158) is in the central basin of the South China Sea (CBSCS) and located in 3573 m water depth on Jiaolong seamount. In addition, we compiled available mineralogical and geochemical data of Fe-Mn nodules and crusts from the northern SCS (Supplement Table A3).

3.2. Mineralogy

Mineralogy was performed by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The samples were first thoroughly examined by transmitted and reflected light microscopy, and the internal structure and micro-textural features were described, outlined and photographed. The XRD equipment used included a PANalytical X'Pert PRO diffractometer, Cu-K α radiation, carbon monochromator and automatic slit (PTRX-004). The analytical conditions for the XRD were: Cu-K α radiation at 40 kV and 30 mA, a curved graphite secondary monochromator, scans from 2 to 70 (2 θ), step size of 0.0170 (2 θ) and step time 0.5°/min. Scanning electron microscopy (SEM-EDS) of morphological and 3D textural mineral characteristics was performed on a Hitachi S-4800 instrument and energy dispersive X-ray (EDX) spectrometer (Oxford X-Max 20); spectra were obtained at 20 kV accelerating voltage, and 2 and 10 nA beam current for the EDX.

3.3. Geochemistry

For major, trace and REE analysis, powder samples of Fe-Mn nodules were prepared as follows. The surface layers of the nodules, 3 mm in thickness, were cut from the 15 samples and approximately 40 mg powder was dried at 105–110 °C and then placed into a Teflon beakers. After 0.5 ml HF, 0.5 ml HNO₃ and 1.5 ml of

HCl were added, the sealed beakers were placed in an electric oven at 180 °C for about 12 h. After cooling, the beakers were heated on a hot plate to dryness, after which 1 ml of HNO₃ and 1 ml of H₂O were added. The beaker was again sealed and placed in an electric oven at 150 °C for about 12 h to dissolve the residue. Major elements were determined using a Thermo-Fisher IRIS II Intrepid XSP ICP-OES. Trace elements and REEs were determined using a Perkin-Elmer ELAN 9000 ICP-MS. All the samples were analyzed at the Institute of Oceanology, Chinese Academy of Sciences (IOCAS).

The sensitivity of the instrument was adjusted to about 30,000 cps (counts per second) for 1 ng/ml ¹¹⁵In. Analysis of the reference materials (GBW07315, GBW07316, BCR-2, BHVO-2, GBW0725, GBW07296, NOD-P-1 and NOD-A-1) which are either sediment, basalt or manganese nodules, gave results typically within $\pm 10\%$ of certified values. Analytical precision, given as the relative standard deviation (RSD), was determined by duplicate analyses of several samples and was typically better than 5%.

In this study, $Ce/Ce^* = 2Ce_{SN}/(La_{SN} + Pr_{SN})$, $Ce_{anomaly} = \log (Ce_{SN}/Ce_{SN}^*)$, and $Eu_{SN}/Eu_{SN}^* = 2Eu_{SN}/(Sm_{SN} + Gd_{SN})$, where SN refers to normalization of concentration against the Post Archean Australian Shale (PAAS; McLennan, 1989). Discrimination plots used PAAS normalized REY data with $Ce^* = 0.5La_{SN} + 0.5Pr_{SN}$ or if Pr data were unavailable $Ce^* = 0.67La_{SN} + 0.33Nd_{SN}$; plots are Ce_{SN}/Ce_{SN}^* vs Nd and Ce_{SN}/Ce_{SN}^* vs Y_{SN}/Ho_{SN} (Bau et al., 2014) to further confirm that the samples used for comparison are hydrogenetic or diagenetic.

The growth rates of Fe-Mn nodules and crusts were calculated using an empirically derived cobalt chronometer: growth rate (GR) = $0.68/(Co^n)^{1.67}$, where $Co^n = Co \times (50/Fe + Mn)$, with Co, Fe, and Mn expressed as weight percent (wt.%) (Manheim and Lane-Bostwick, 1988). One limitation of this method is that the equation does not take into account possible hiatuses during the accretion process. Therefore, the calculated rates represent maximum values and the derived age minimum values (Hein et al., 1990).

Table 1

Location, setting, and description of ferromanganese nodules and crusts from northern South China Sea.

Location	Longitude	Latitude	Depth(m)	Types	Substrate	Morphology	Mineralogy	Reference
<i>Northeastern SCS (Province A)</i>								
05E105	116°21.543'	20°37.256'	472	Nodule	Siliceous ooze	Irregular to spherical	Goethite, quartz, clay minerals, CFA	This study
05E204	117°57.087'	20°59.130'	1370	Nodule	Siliceous ooze	Cylindrical and spherical	Goethite, barite, pyrite, quartz and clay minerals	
10E204B	117°57.3142'	21°0.1629'	1331	Nodule	Siliceous ooze	Irregular and cylindrical	Goethite, quartz, clay minerals	
ZX31	118°0.59'	21°32.79'	1000	Nodule	Siliceous ooze	Rodlike, irregular and cylindrical	Goethite, barite, quartz, clay minerals	
SA1–28	118°16'	21°11'	2000	Nodule	Siliceous ooze	Concretion and rodlike	δMnO ₂ , goethite, quartz, clay minerals	Lin et al. (2003)
82–23	118°0.07'	21°31.12'	1656	Nodule	Siliceous ooze	Concretion and rodlike	Sodium manganite and todorokite	Liang et al. (1988)
<i>Northwestern SCS (Province B)</i>								
05E107	117°09.528'	19°46.430'	2255	Nodule	Siliceous ooze	Spherical	Todorokite, birnessite, quartz, albite	This study
09KJ22	112°59.716'	17°1.591'	1501	Nodule	Siliceous ooze	Spherical	CFA, asbolane, todorokite, birnessite, barite	
SO4–1DG	113°05.3857'	17°54.9122'	1700	Nodule	Siliceous ooze	Spherical, kidney, irregular	Vernadite, quartz, chlorite, illite, albite	Zhang et al. (2013)
SO4–7DG	115°24'	17°03'	1200	Nodule	Siliceous ooze	Spherical, irregular	Quartz, Vernadite, plagioclase and calcite	
KD18	115°21'	18°28'	3400	Nodule	Siliceous ooze	Spherical, tabular and irregular	10 Å manganates, δMnO ₂	Bao and Li (1993)
KD20	115°24'	17°01'	1070	Nodule	Siliceous ooze	Spherical, tabular and irregular	10 Å manganates, δMnO ₂	
KD23	114°36'	16°46'	1400	Nodule	Siliceous ooze	Spherical, tabular and irregular	10 Å manganates, δMnO ₂	
KD35	113°03'	17°01'	1500	Nodule	Siliceous ooze	Spherical, tabular and irregular	10 Å manganates, δMnO ₂	
KD17	115°21'	18°54'	2470	Crust	Siliceous ooze	Tabulate, oolitic texture on the surface	10 Å manganates, δMnO ₂	
KD21	114°23'	16°56'	2170	Crust	Siliceous ooze	Tabulate, oolitic texture on the surface	10 Å manganates, δMnO ₂	
KD29	114°58'	16°04'	1250	Crust	Siliceous ooze	Tabulate, oolitic texture on the surface	10 Å manganates, δMnO ₂	
<i>Central Basin SCS (Province C)</i>								
J–158	117°45.206'	17°33.696'	3570	Nodule	Basalt	Spherical	Birnessite, todorokite and asbolane	This study
40TKD	118°48.9'	12°21.4'	1000	Crust	Volcanic rock	–	δMnO ₂	Chen and Cui (1998)
44TKD	118°51.6'	12°48.5'	1900	Nodule	Volcanic rock	–	δMnO ₂	
Xianbei	116°50'	16°40'	3000	Crust	Volcanic rock	–	Manganite and δMnO ₂ , feldspar and calcite	
8#	116°59'	17°37'	3429	Crust	Basalt	–	Todorokite, clay mineral, feldspar, pyroxene	Yao et al. (1986)
9#	116°30'	14°48'	3116	Crust	Basalt	–	Todorokite, clay mineral, feldspar, pyroxene	
10#	115°35'	14°00'	3014	Crust/nodule	Volcanic rock	–	Todorokite, clay mineral, feldspar, pyroxene	
S–9	118°30'	15°00'	1000	Crust	–	–	–	Wang et al. (1984)
S–10	115°06'	14°00'	3000	Crust	–	–	–	
Jianfeng	116°25'	19°28'	1500	Crust	Volcanic rock	Oolitic and kidney shape	Todorokite, δMnO ₂ , bernadite, birnessite	Liang et al. (1991)
SO4–12DG	116°09.5602'	15°34.3202'	1290	Nodule	Basalt	Irregular shape	Quartz, vernadite, mica, calcite, illite, smectite	Zhang et al. (2013)

4. Results

4.1. Structure and textural features

The studied nodules in the NESCS show a wide range of sizes, colors and morphologies. The most abundant samples range in size from 2 to 4 cm and have an ellipsoidal or spherical shape, although there are nodules up to 8 cm in diameter with a tabular-to-irregular shape. The external color of these Fe–Mn nodules ranges from yellow-orange to black, with red-brown being the most usual color (Fig. 4a–c). Some encrusting organisms, such as tubeworms were observed on nodules surface (Fig. 4b). Internally, the nodules

show a complex arrangement of layers with indications of oxidation, open fracture discontinuities and beige phosphorite lenses (Fig. 4c).

The nodules of the NWSCS display different morphologies, including tabular, irregular, discoidal, ellipsoidal, with tabular being the most abundant; the surface texture is smooth. Unlike the Fe-rich nodules from the NESCS, the surface color varies between brown and black and the diameter of nodules ranges from 2 to 10 cm. The nodules are characterized by subparallel growth layers around the nucleus (Fig. 4d and e). The layers are massive to thinly laminated and the nucleus-layer boundary is diffuse and paler in color than the laminae (Fig. 4e). Discontinuities in

Fig. 4. Fe-Mn nodules and sub-samples, from the northern SCS analyzed in this study. (a–c) Fe-rich nodules from the NESCS; (d and e) Fe-Mn nodules from NWSCS; (f) Fe-Mn nodule from the CBSCS.

the layers were not observed at the macroscopic level. Coalescence of spheroidal nodules formed sub-spheroidal to tabular nodules.

The J-158 nodule sample in the CBSCS show the same surface colors, sizes, morphologies and internal structure as the NWSCS nodules. The most abundant morphology is ellipsoidal. The surface texture is relatively rough botryoidal and the nodule edges are rounded (Fig. 4f). Mottled textural features were observed internally in some nodule.

4.2. Mineralogy

XRD results of the Fe-Mn nodules and crusts are summarized in the Table 1. The oxyhydroxide minerals show strong overlaps and low crystallinity (Fig. 5). Goethite is the most dominant mineral in all samples from the NESCS. Petrographic and SEM images reveal botryoidal textures and fine aggregates of goethite forming rosettes in groups (Figs. 6a and 7a and b). Other main components of the nodules are: detrital quartz and clay minerals (muscovite, smectites, illite). Clay minerals seem to have two different origins based on SEM images, detrital minerals and authigenic phases (Fig. 7c). Authigenic barite is a main component in nodules from the 05E204 station. Accessory minerals accompanying these major phases include authigenic pyrite and detrital anorthite. Authigenic carbonate fluor-apatite (CFA) and carbonate hydroxyl-apatite are abundant in nodules from the 05E105 station (Fig. 7b). The SEM images show well-developed clusters of idiomorphic authigenic CFA crystals filling foraminifera chambers (Fig. 6d).

The main components of the nodules from the NWSCS are: Mn oxides, barite and CFA as authigenic phases and detrital quartz, albite and phyllosilicates (Fig. 5c and e). Mn oxides are birnessite (7 Å manganates) and todorokite (10 Å manganates); their characteristic peaks are found in the area of higher spacing and in broadening of the peaks identified in the diffractograms. Birnessite and todorokite show some characteristic peaks at 7.08 Å for birnessite and 9.4 Å for todorokite, with the maximum intensity peak at 4.74 Å. Minor amounts of asbolane and coronadite, which are usually inter-grown, can also be recognized on XRD. Petrographic SEM images show botryoidal textures in Mn oxides with mineral grain sizes smaller than SEM resolution (Fig. 6b, d and e). Accumulations of carbonate coccolith shells are observed in some nodules. Large clusters of authigenic CFA idiomorphic crystals are common in samples from the 09KJ22 station (Fig. 7h). Dispersed authigenic crystals of barite are seen under the electron microscope (Fig. 7g).

SEM shows bacteria films: (1) micrometer size tubular, helically fibrous structures less than 2 µm in diameter, (2) coccoid spheroidal structures, and (3) rod-shape forms covered by Fe-Mn oxides, that may result from the activity of microorganisms (Fig. 6e and f).

The nodule J-158 from the CBSCS is mainly composed of birnessite and todorokite inter-grown with minor amounts of asbolane (Fig. 5f), all forming botryoidal textures under the petrographic and electron microscope (Figs. 6c and 7i). Detrital quartz, anorthite and phyllosilicates (illite and montmorillonite) are also major phases.

4.3. Geochemistry

The bulk chemical composition of the Fe-Mn deposits is provided in Table 2. Fe (up to 45.5 wt.%) is the most abundant element in the nodules from the NESCS, followed by Al, Mg, P and Ca. Mn contents are very low (~0.03 wt.%). The abundance of Al (up to 3.69 wt.% Al_2O_3) suggests the presence of clay minerals in the nodules as confirmed by XRD and SEM. The Mn/Fe ratios vary from 0.001 to 0.13 with a mean value of 0.03. Some nodules from the 05E105 station show high P_2O_5 contents (up to 3.7 wt.%) indicating the abundance of phosphate minerals. The combined Cu + Ni + Co concentration is very low ranging from 0.01 to 0.19 wt.% with an average of 0.07 wt.%, which is very depleted compared with the mean value for oceanic abyssal nodules (1.4 wt.%) (Baturin, 1988). Ba, V, Zn, Pb, and Cr are the most abundant trace metals on the NESCS nodules. The markedly high Ba content in nodule 05E204-1 likely reflects the abundance of barite in detrital grains and authigenic minerals. Nodule 10E204B-1 shows moderate contents of Ce, Co and other trace metals, indicating combined genetic processes (diagenesis and hydrogenesis) for this nodule. All Fe-Mn nodules from the NESCS show very low total REE contents (157.7 µg/g on average) ranging from 29.8 to 441.3 µg/g (Table 2). They show a moderate enrichment in light rare earth elements (LREEs) and a negative to slightly positive Ce anomaly ($\text{Ce}/\text{Ce}^* = 0.88\text{--}1.95$) and a positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 1.08\text{--}1.16$). For seven samples of Fe-rich nodules, P has a positive correlation with Ca (0.94). The terrigenous elements Al, K, Na and Ti show positive correlations among members of that group (0.6–0.9). Fe exhibits a positive correlation with Mg (0.77) and a negative correlation with Na (−0.95) (Supplement Table A1).

Bulk average element contents in nodules from the NWSCS show a different pattern. Fe and Mn display similar average con-

Fig. 5. (a and b) The XRD profiles for NESCS Fe-rich diagenetic nodules; (c–e) NWSCS hydrogenetic-diagenetic Fe-Mn nodules; (f) CBSCS Fe-Mn nodules. Qtz = quartz, CFA = carbonate fluorapatite, Tod = todorokite, Bir = birnessite, Asb = asbolane, Goe = goethite, Bar = barite, Pyr = pyrite, Mos = muscovite, Alb = albite, Anor = anortite, Clin = clinoclone, Ed = edentite (amphibole).

Fig. 6. Polished-section and SEM biomimneralization photomicrographs of Fe-Mn nodules from the northern SCS. (a) Minute pyrite, yellow in color, dispersed in a goethite mosaic with abundant detrital grains; (b) Botryoidal layered texture of Fe-Mn oxyhydroxides with detrital minerals concentrated between the columns; (c) Mn rich oxyhydroxides (todorokite and birnessite) inter-grown; (d) Bacteria-related biofilms (fibrils, rod-shaped and mats) covering CFA authigenic crystals; (e, f) Filamentous and helical fibrils bacteria covered by Fe-oxyhydroxides. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. 3D scanning electron microscope (SEM) micrographs of textural features of nodules mineralogical components. (a) Idiomorphic CFA crystal surrounded by goethite; (b) Clusters of goethite roses in Fe-rich nodules from the NESCS; (c) Authigenic plates of smectite; (d and e) Botryoidal Fe-Mn oxyhydroxide laminations in nodules from the NWSCS; (f) Todorokite minute crystals; (g) Foraminifera chambers filled by authigenic CFA and dispersal barite (red arrows); (h) Detail of idiomorphic CFA crystals forming columnar clusters in foraminifera chambers; (i) Mn oxide laminations in Fe-Mn nodules from the CBSCS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

centrations: 12.1 and 14.2 wt.%, respectively. The Mn/Fe ratios vary from 0.77 to 1.67 with a mean of 1.21. The high content of Al_2O_3 (up to 5.56 wt.%) reflects clay minerals within the nodules. The mean total concentration of Cu + Ni + Co in bulk nodules is 0.72 wt.%, with values ranging from 0.47 to 1.06 wt.%. Two nodules show high P_2O_5 concentrations (around 6.5 wt.%) indicating the abundance of phosphate minerals. Samples show moderate contents of TiO_2 (up to 0.6 wt.%). There are also high concentrations of Ba, Pb, Sr, Zn and Zr (Table 2). Fe-Mn nodules from the NWSCS show moderate to high REE concentrations ranging from 876.6 to 1378.0 $\mu\text{g/g}$, with positive Ce and Eu anomalies. For seven Fe-Mn nodule samples from this province, the biogenic element P, Ca, Sr and Ba show strong positive correlations among members of that group (>0.95). Fe exhibits a positive correlation with Ti (0.97) and a negative correlation with Mn (−0.93). Ca shows a negative correlation with Al (−0.96) and Na (−0.83) (Supplement Table A2).

The nodule J-158 collected in the CBSCS has 13.6 wt.% Mn and 9.36 wt.% Fe, with Mn/Fe of 1.45 (Table 2). Al_2O_3 (8.23 wt.%) is more abundant than in the nodules collected on the slopes (NESCS and NWSCS). The Cu + Ni + Co concentration is 0.66 wt.%. The most abundant trace metals are Ba, Pb, Zn and V, with high content of Li (64 $\mu\text{g/g}$). In the nodule from the CBSCS (J-158), the REE concentrations are moderate (620.6 $\mu\text{g/g}$) with relatively low Ce (399 $\mu\text{g/g}$) content, and positive Ce ($\text{Ce}/\text{Ce}^* = 2.72$) and Eu anomalies ($\text{Eu}/\text{Eu}^* = 1.2$). Y is specially enriched in Fe-Mn samples from the NWSCS and CBSCS relative to the nodules from the NESCS.

All samples are enriched in LREEs compared with heavy rare earth elements (HREEs; $\text{LREE}/\text{HREE} = 5\text{--}25$), but this enrichment is more apparent in the Fe-Mn nodules from the NWSCS and CBSCS

($\text{LREE}/\text{HREE} = 12\text{--}25$). PAAS-normalized REE in this study show a flat pattern, indicating that terrigenous material contributes to the REE enrichment (Fig. 10); however, correlations coefficients show that the Fe phase is the predominant host for REE in NWSCS (positive correlation with Fe, and negative correlations with Al and Mn), and Mn is the predominant host for REE in the NESCS, with a positive correlation with Mn and no correlations with Al or Fe (Supplement Tables A1 and A2). For other samples from the global ocean, the light REE are depleted relative to the heavy REE.

4.4. Growth rates

As most of the samples show Co contents below 0.4 wt.%, the Co chronometer used was the [Manheim and Lane-Bostwick \(1988\)](#) equation which uses Fe, Mn and Co contents in the samples. The GR in nodules from the northern SCS are variable, ranging from 4.6 to 17,408 mm/Myr for nodules from the three areas analyzed here. The Fe-rich nodules from the NESCS have the highest GR (47–17,408 mm/Myr) and an average GR of 3320 mm/Myr. The average GR in the Fe-Mn nodules from the NWSCS is 7.1 mm/Myr. Nodule J-158 from CBSCS has a GR of 6.5 mm/Myr. Diagenetic and hydrothermal Fe-Mn deposits growth rates that can be very fast. For example, Fe-Mn nodules from the Peru Basin have GR up to 250 mm/Myr ([von Stackelberg, 2000](#)), and up to 24,000 mm/Myr for hydrothermal deposits (e.g., [Hein et al., 1990](#)). For the hydrothermal deposits and Fe-rich diagenetic nodules formed subsurface, this means that deposit formation was rapid and short lived.

Table 2
Chemical composition of selected northern SCS Fe-Mn nodules and crusts.

Area Location	NESCS							NWSCS							CBSCS J158
	05E204-1	05E204-2	10E204B-1	10E204B-3	05E105-2-18	05E105-2-19	ZX31-1	05E107-1	05E107-3	05E107-5	05E107-6	05E107-7	09KJ22-3-1	09KJ22-3-2	
Fe (wt.%)	36.0	41.5	34.2	40.9	45.4	43.0	29.8	14.5	14.3	12.0	10.0	10.5	11.3	12.4	9.36
Mn	1.17	0.76	4.77	0.25	0.17	0.11	0.04	12.2	12.0	16.2	18.1	18.4	14.8	16.2	14.7
Al ₂ O ₃	3.27	2.10	2.09	2.35	1.85	2.21	3.69	4.64	4.54	5.00	5.56	5.00	2.57	2.73	8.23
CaO	0.71	0.64	1.03	0.53	1.49	4.78	0.43	1.69	1.72	1.65	1.43	1.76	10.21	11.08	2.27
K ₂ O	0.59	0.30	0.39	0.45	0.34	0.47	1.37	0.80	0.80	1.02	1.16	1.06	0.80	0.90	1.19
MgO	1.36	1.76	1.72	1.47	1.93	1.85	1.50	1.73	1.79	2.33	2.58	2.43	1.62	1.86	2.90
Na ₂ O	0.62	0.45	0.81	0.38	0.27	0.31	0.87	2.23	2.05	2.11	2.01	2.18	1.82	1.90	2.38
P ₂ O ₅	0.92	1.73	1.53	1.13	1.46	3.70	0.50	0.61	0.63	0.53	0.42	0.49	6.59	6.68	0.36
TiO ₂	0.23	0.14	0.20	0.15	0.14	0.17	0.21	0.60	0.59	0.48	0.43	0.42	0.45	0.48	0.46
Co (μg/g)	226.7	186.7	611.3	197.8	101.1	19.8	35.4	1647.6	1504.8	1328.7	1533.0	1106.0	1357.9	992.2	1190.3
Ni	501.1	356.9	1051.1	575.7	260.5	102.4	39.3	2766.7	3206.2	6580.6	7582.3	8555.0	3886.9	2883.3	4172.5
Cu	83.6	65.3	216.3	38.6	6.0	4.8	24.9	523.1	462.5	733.0	961.4	955.6	782.5	810.5	1199.2
Zn	351.1	574.6	604.4	371.7	137.3	111.2	146.7	479.6	508.5	640.8	711.7	838.1	653.5	663.3	584.2
Pb	485.7	224.3	960.7	162.9	63.5	68.2	97.8	2218.3	2255.3	1626.1	1279.5	1407.1	2262.5	1953.9	885.7
Ba	6800.8	111.4	349.8	107.1	53.1	65.1	170.5	1005.3	1034.9	1213.0	1327.7	1136.1	10390.5	11139.8	1084.2
Sr	368.0	154.9	369.0	125.9	89.9	204.5	131.7	842.6	861.5	757.0	635.1	695.7	2539.7	2024.4	540.1
Mo	35.3	18.4	43.8	35.7	21.2	25.6	20.7	67.6	51.3	57.8	71.1	107.7	55.2	115.2	64.6
V	400.6	1099.9	1137.4	445.4	271.4	258.8	293.1	371.9	369.5	372.6	365.0	376.3	679.8	475.5	323.2
Hf	2.55	1.83	3.30	1.39	0.70	0.80	0.90	8.52	9.34	6.80	5.33	5.66	4.81	4.22	4.26
Ta	0.24	0.14	0.20	0.17	0.19	0.23	0.28	0.42	0.45	0.41	0.40	0.38	0.46	0.40	0.34
Th	13.4	8.06	21.4	6.33	3.61	5.06	5.34	63.9	71.7	56.0	45.5	47.0	63.4	61.6	37.9
U	4.60	2.88	4.47	3.35	5.43	9.82	8.65	5.10	4.97	4.22	3.54	4.24	8.35	7.94	2.51
Cr	447.0	357.2	157.3	256.9	153.5	65.9	152.3	23.9	25.5	26.7	29.6	26.3	11.5	11.1	31.6
Ga	8.47	5.02	6.94	4.88	3.88	4.29	5.57	12.8	13.7	15.3	18.7	17.3	12.8	16.9	17.8
Rb	31.3	14.4	17.4	23.0	20.1	23.8	51.4	24.0	25.5	32.0	38.1	33.5	15.2	14.7	36.4
Zr	122.9	101.5	172.2	69.8	32.8	34.0	42.4	690.8	700.7	487.8	285.7	304.6	288.5	263.3	226.7
Nb	12.0	8.99	14.17	6.90	6.43	5.99	4.68	37.5	38.1	27.7	23.1	23.8	35.4	31.4	15.1
Cs	2.65	1.12	1.39	1.89	1.81	1.97	3.44	1.73	1.83	2.39	2.84	2.49	0.95	0.85	2.72
Li	16.8	11.4	15.6	13.8	6.1	7.0	16.3	19.4	20.3	37.3	43.9	48.7	11.6	11.2	63.7
Sc	5.82	6.48	5.58	2.74	1.15	1.11	1.82	13.01	12.90	9.91	9.91	9.50	8.28	4.49	12.86
Mn/Fe	0.03	0.02	0.13	0.01	0.00	0.00	0.00	0.76	0.76	1.22	1.63	1.58	1.18	1.18	1.42
GR	229.8	394.4	47.0	344.0	1252.5	17408.8	3566.3	4.55	5.18	7.03	5.46	9.88	5.97	11.78	6.46
La	39.0	25.1	62.4	20.6	6.5	15.8	18.5	155.2	155.5	113.8	109.5	124.7	90.5	105.6	69.0
Ce	110.2	74.0	252.7	45.2	11.0	41.3	31.6	796.8	882.2	640.3	546.3	561.6	810.0	1188.0	398.9
Pr	8.38	5.05	14.24	4.07	1.28	2.48	3.46	37.82	38.44	29.42	24.38	25.84	23.41	22.58	16.58
Nd	33.8	20.1	57.8	16.4	5.1	10.5	13.9	158.8	160.8	125.5	103.7	108.8	92.7	87.2	69.4
Sm	7.33	4.57	13.16	3.47	1.04	2.21	2.86	36.20	36.13	28.71	24.03	25.48	20.93	19.75	16.00
Eu	1.70	1.07	3.16	0.85	0.25	0.55	0.65	8.88	8.50	6.97	6.04	6.18	4.65	4.27	4.06
Gd	7.35	4.40	12.44	3.38	1.10	2.42	2.66	35.46	35.02	27.48	22.56	24.17	23.46	22.15	15.69
Tb	1.06	0.73	1.96	0.54	0.19	0.42	0.44	5.51	5.18	4.23	3.43	3.70	2.97	2.82	2.44
Dy	5.25	3.88	9.89	3.13	1.14	2.57	2.47	26.97	25.19	20.73	16.61	18.73	14.03	12.94	12.30
Y	24.1	19.4	41.0	17.8	10.5	20.9	12.9	85.0	81.6	62.0	51.1	60.4	51.1	60.4	76.7
Ho	1.07	0.83	2.02	0.65	0.28	0.62	0.51	5.32	4.90	3.88	3.12	3.54	2.79	2.77	2.44
Er	2.84	2.27	5.24	1.82	0.81	1.75	1.43	13.38	11.94	9.43	7.84	9.15	7.39	7.11	6.20
Tm	0.43	0.37	0.78	0.29	0.13	0.27	0.22	2.01	1.78	1.40	1.13	1.33	1.12	1.09	0.95
Yb	2.69	2.45	4.79	1.89	0.80	1.65	1.42	11.92	10.70	8.19	6.83	7.97	6.80	6.60	5.78
Lu	0.42	0.38	0.74	0.30	0.14	0.26	0.22	1.89	1.70	1.26	1.03	1.18	1.07	1.07	0.86
LREE	200.4	129.9	403.5	90.6	25.2	72.9	71.0	1193.8	1281.5	944.7	814.0	852.6	1042.2	1427.3	573.9
HREE	21.1	15.3	37.9	12.0	4.59	9.97	9.38	102.5	96.4	76.6	62.6	69.8	59.6	56.6	46.7
LREE/HREE	9.50	8.48	10.7	7.54	5.49	7.31	7.57	11.7	13.3	12.3	13.0	12.2	17.5	25.2	12.3
REE	221.5	145.3	441.3	102.6	29.8	82.8	80.4	1296.2	1377.9	1021.3	876.6	922.4	1101.8	1483.9	620.5
Ce/Ce*	1.41	1.52	1.95	1.13	0.88	1.49	0.91	2.40	2.63	2.55	2.44	2.28	4.05	5.61	2.72
Ce _{anomaly}	0.15	0.18	0.29	0.05	−0.05	0.17	−0.04	0.38	0.42	0.41	0.39	0.36	0.61	0.75	0.43
Eu/Eu*	1.09	1.12	1.16	1.16	1.08	1.10	1.11	1.16	1.12	1.17	1.22	1.17	0.98	0.95	1.20
Y _{SN} /Ho _{SN}	0.83	0.86	0.75	1.01	1.40	1.25	0.92	0.59	0.61	0.59	0.60	0.63	0.67	0.80	1.15

Calculated according Bau et al. (2014).

5. Discussion

5.1. Province characteristics of Fe-Mn nodules and crusts on the seafloor

Fe-Mn nodules and crusts are found in a wide variety of oceanographic and tectonic settings. Accordingly, based on the formation environment, the northern SCS is divided into three Fe-Mn nodules provinces: the NESCS (Province A), NWSCS (Province B) and CBSCS (Province C, Fig. 1b). The most prominent physiographic features of the northern SCS are mud volcanoes and hydrocarbon seep structures located along the northeast margin (Chen et al., 2005), the Luzon Strait through which NPDW undercurrent circulates (Qu et al., 2006a), and widely distributed volcanic seamounts that formed after the cessation of seafloor spreading (Chung et al., 1997; Zhou et al., 2009). The field sites, morphology, mineralogical and geochemical data from this study and previous studies allow us to propose a comparison with other deep-seabed polymetallic nodules and shallow-water and continental margin nodules from other ocean basins and tectonic settings around the world. Moreover, based on these data we can discuss the different provincial characteristics of nodules and crusts growth in the oceanographic and geotectonic contexts of the northern SCS.

5.1.1. Province A (NESCS)

The nodule fields in Province A occur at the base of seepage mounds, where the influence of the NPDW is strong and where extensive hydrocarbon-rich fluid venting and mud diapirs are observed, which includes numerous mud volcanoes, methane-related authigenic carbonates (crusts, chimneys), gas hydrates and pockmarks (Fig. 2a) (Han et al., 2013; Li et al., 2013b; Wang et al., 2014; Zhang et al., 2015). These geological and environmental conditions of Fe-Mn nodule fields on the NESCS are very similar to the occurrences in the Gulf of Cadiz (González et al., 2010, 2012).

The nodules physical properties such as maximum diameter, density, and weight are similar to nodules reported to occur in the shallow-waters and continental margins in the Baltic Sea, the Gulf of Finland, Black Sea and the Gulf of Cadiz (e.g., Hlawatsch et al., 2002; González et al., 2007; Zhamoïda et al., 2007; Baturin, 2010). Rodlike, irregular and concretion morphologies are predom-

inant in the Province A nodules (Table 1) as in other shallow water nodules such as those reported from the Gulf of Cadiz (González et al., 2007). Otherwise, cylindrical nodules are similar to the tabular concretions formed around burrows reported in the Black Sea (Baturin et al., 2002). The NESCS nodules are characterized by Fe oxyhydroxides (goethite type) predominating over Mn oxides unlike those in deep-sea nodules where Mn oxides are predominant (e.g., Hein et al., 2013). The silicates (clay minerals) present in the nodules are distinctive from the mud sediments with different sources than those of the hemipelagic samples. The abundance of clay minerals (especially smectite) are therefore characteristic of the nodules, and directly related to the fluid venting processes. Authigenic pyrite, barite and CFA in nodules reflect fluctuations in the redox boundaries probably associated with microbial cycles of metals in the seabottom sediments affected by hydrocarbon seeps (Vanneste et al., 2013).

Unlike oceanic polymetallic nodules (Chandnani et al., 2012; Hein et al., 2012; Węgorzewski and Kuhn, 2014), Province A samples plot in an area with high Fe content (13.0–45.5 wt.%), low to moderate Mn content (0.03–12.4 wt.%), and very low Cu + Co + Ni concentrations (0.01–0.76 wt.%; Fig. 8, Table 3 and Supplement Table A3). The Mn/Fe ratio is 0.002–0.95, well below the Mn/Fe ratio of typical oceanic polymetallic nodules. The PAAS-normalized trace elements patterns show moderate enrichments in Mo, Pb, Ba, Co, Ni, V and Cr (Fig. 9a). The total REE concentrations range from 29.8 to 441 µg/g, with no and slight positive Ce anomalies ($Ce/Ce^* = 0.88–1.51$) and positive Eu anomalies ($Eu/Eu^* = 1.08–1.16$, Fig. 10a). All Fe-Mn nodule and crust layers have a small (1.11–1.29) positive shale-normalized Eu anomaly that most likely reflects that of seawater (Bau et al., 1996). However, for the Fe-rich nodules studied here, which likely formed subsurface, contained barite may also contribute to the positive Eu anomalies. In general, the REE contents of the NESCS Fe-Mn nodules are similar to modern seep carbonates in the Dongsha and Congo fans and hydrocarbon-derived Fe-Mn nodules and carbonate chimneys from the Gulf of Cadiz (Fig. 10d) (Feng et al., 2009; Ge et al., 2010; González et al., 2010; Magalhães et al., 2012). The REE in the most deep-ocean Fe-Mn deposits are hosted by the Fe and Mn phases and the total REE contents decrease with increasing diagenetic contributions (Hein and Koschinsky, 2013).

Fig. 8. Contents of Fe, Mn, Cu, Co and Ni for ferromanganese oxides from the study area. The fields are: (A) NESCS, (B) NWSCS, (C) CBSCS. Ocean basins: NW Pacific (Hein et al., 2012), Indian Ocean (Chandnani et al., 2012) and Clarion-Clipperton Fracture Zone (Węgorzewski and Kuhn, 2014).

Table 3

Abundance (weight percent) of important elements in manganese nodules by province in the northern South China Sea.

Physiographic Province		Ni + Cu + Co (wt.%)	Mn/Fe	Mn	Fe	Co	Ni	Cu	ΣREE (μg/g)
Province A	Min	0.01	0.002	0.033	13.0	0.002	0.004	0.0005	29.8
	Max	0.76	1.08	12.4	45.5	0.24	0.56	0.09	441
	mean	0.23	0.95	3.26	32.1	0.08	0.11	0.03	158
Province B	Min	0.34	0.54	8.90	10.0	0.08	0.18	0.03	841
	Max	2.96	1.67	17.0	20.4	0.23	0.86	2.48	2771
	mean	0.79	0.90	13.4	15.7	0.15	0.38	0.26	1530
Province C	Min	0.35	0.75	12.4	9.4	0.11	0.20	0.03	620
	Max	1.21	2.05	23.8	17.2	0.42	0.94	0.13	1524
	mean	0.81	1.35	17.8	13.6	0.21	0.52	0.08	1203

Min = minimum; Max = maximum.

Fig. 9. PAAS-normalized trace element patterns of (a) NESCS (Province A); (b) NWSCS (Province B) and (c) CBSCS (Province C) samples in the northern SCS. **Fig. 10.** Comparison of PAAS-normalized rare earth elements patterns for bulk nodules from (a) NESCS (Province A); (b) NWSCS (Province B); (c) CBSCS (Province C); (d) Vent-related precipitates and fluids; (e) Hydrothermal hydroxides; (f) From elsewhere (Hein et al. (2000) and Hein and Koschinsky (2013)).

5.1.2. Province B (NWSCS)

The nodule and crust fields are distributed on the northern slope of the SCS where the NPDW influence is stronger than in Province A and C. The deep water (>2000 m) currents of the SCS which are strongest along the SCS slope (Lüdmann et al., 2005; Shao et al., 2007; Gong et al., 2012), promote nodules and crusts formation,

enhance turbulent mixing, and produce upwelling, leading to increased primary productivity and the maintenance of an oxygen minimum zone (Hein et al., 2010).

Province B covers a broad area, including extensive areas of Fe-Mn nodules and sporadic crusts. Spherical, tabular to irregular morphologies predominant in the northern slope are similar to

nodules reported to occur in the Pacific (Hein et al., 2012) and Indian Ocean basins (Pattan and Parthiban, 2011; Pattan et al., 2013). The scattered Fe-Mn crusts are mostly distributed around Zhongsha and Xisha carbonate platforms. Previous studies of hydrogenetic nodules show strong similarities with hydrogenetic Fe-Mn crusts in the NWSCS with respect to both mineralogical and chemical compositions, reflecting largely identical mechanisms of formation (Bao and Li, 1993). Nodules and crusts from Province B are characterized by moderate Fe and Mn contents (~9–20 wt.%) and are more enriched in Cu, Co and Ni (Table 3 and Supplement Table A3) than Province A samples. The chemical composition of the Province B Fe-Mn nodules is different from the Indian Ocean (Mukhopadhyay et al., 2003) and CCFZ nodules (Wegorzewski and Kuhn, 2014), but relatively close to the north-west Pacific nodules (Hein et al., 2012) (Fig. 8). The PAAS-normalized trace elements patterns of NWSCS nodules are strongly enriched in Mo, Pb, Co, Ni and Cu and moderately depleted in V, Rb and Cr (Fig. 9b). The total REE concentrations range from 841 to 2771 $\mu\text{g/g}$ (Table 3 and Supplement Table A3), with positive Ce ($\text{Ce}/\text{Ce}^* = 2.06\text{--}5.61$) and Eu ($\text{Eu}/\text{Eu}^* = 0.89\text{--}1.48$) anomalies (Fig. 10b). Marine authigenic Fe-Mn oxyhydroxides of hydrogenetic origin commonly show positive Ce anomalies owing to the oxidation of Ce^{3+} to Ce^{4+} in seawater and its subsequent uptake as CeO_2 by metalliferous nodules or crusts (Piper, 1974; Nath et al., 1992). As with the NESCS samples, the NWSCS nodules with a positive Eu anomaly most likely reflects that of seawater and contained barite. The enrichment of trace metals of economic interest in Fe-Mn nodules and crusts is particularly important for their potential as a strategic resource, because of the high concentrations of REE (Fig. 10). CFA that forms phosphorites also hosts REE in a wide variety of environments along continental shelves and slopes of Pacific and Atlantic oceans (Hucrrns et al., 1991; Hughes and Rakovan, 2015). CFA concentrates REE during its formation through early diagenetic processes. However, these continental-margin phosphorites typically have lower total REE contents than do Fe-Mn nodules (Hein et al., 2016). Mass-balance considerations indicate that most of REE are hosted by the oxide phases rather than the apatite minerals found in these NWSCS and NESCS nodules. In support of this, the correlation coefficients show no correlations between REEs and P (Supplementary Table A2).

5.1.3. Province C (CBSCS)

The largest region for manganese accumulations in the northern SCS is a broad belt of deposits in the central basin, where bottom roughness is highly variable. Nodule and crust deposits appear to be concentrated between ~1000 m and >3000 m water depths and are particularly abundant in the deepest parts of the central basin, extending into the Zhongnan faults zone between about 14 and 16°N. The Province C deposits are mostly Fe-Mn crusts widely distributed on the volcanic seamounts that formed after the cessation of the seafloor spreading in the basin (Fig. 1; Yao, 1996), such as Daimao Seamount (8# station), Xianbei Seamount (Xianbei station), and Zhenbei Seamount (9# station). Chemical and mineralogical composition of the Fe-Mn nodules and crusts indicate that they have similar geochemical characteristics and occasionally occur together in the same area (e.g., Site 10#, Fig. 1b, Table 1). Most known major seamounts are along, or to the north of, the relict spreading center in the southwest sub-basin (Fig. 2b) and are composed mainly of alkali basalts with subordinate tholeiites that display oceanic island basalt-type geochemical characteristics (Xu et al., 2012). These seamounts and ridges have characteristics that promote development of Fe-Mn crusts and the adsorption of metals from cold seawater, with possible contributions from submarine volcanism/hydrothermal venting.

All the Fe-Mn nodules and crusts are composed predominantly of todorokite and X-ray amorphous iron oxyhydroxide. Mn contents of CBSCS Fe-Mn nodules and crusts vary widely (12.4–23.8 wt.%) with total Cu, Ni and Co concentrations of 0.35–1.21 wt.%, which are close to the range for Province B deposits, Indian Ocean nodules (Mukhopadhyay et al., 2003), and the north-west Pacific Ocean nodules (Hein et al., 2012) (Fig. 8, Table 3 and Supplement Table A3). The PAAS-normalized trace elements patterns show enrichment in Mo, Co, Ni, Cu, and moderate to strong depletion in V, Cr and Rb (Fig. 9c). The total REE concentrations range from 620.6 to 1524.1 $\mu\text{g/g}$, with positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 2.28\text{--}3.14$) and Eu ($\text{Eu}/\text{Eu}^* = 1.01\text{--}1.20$) anomalies (Fig. 10c), which are similar to oceanic hydrogenetic nodules and crusts (Fig. 10f; Bau et al., 1996; Hein and Koschinsky, 2013).

5.2. Proposed genetic model of the Fe-Mn nodules and crusts

Numerous authors have described Fe-Mn concretions associated with a contourite depositional system (CDS) in relation to their typology (nodules, micronodules, laminations and crusts) or their geological and oceanographic context (e.g., Stow et al., 2002). However, few reported references link the geochemistry of Fe-Mn concretions and a CDS (González et al., 2012). Contour currents and their deposits are related to continental margins in all of the ocean basins. The CDS often coincides with areas affected by deep-seated fluid venting (mud volcanism and diapirism), as occurs in the Gulf of Cadiz, Brazil Basin, Gulf of Mexico, Argentine Atlantic margin, Alboran Sea and SCS (Díaz-del-Río et al., 2003; Chen et al., 2005; Hernández-Molina et al., 2006, 2010; González et al., 2007; Magalhães et al., 2012; Somoza et al., 2012). Furthermore, the SCS is also affected by different structures and deposits related to fluid venting and their hydrocarbon-derived carbonates and authigenic barite deposits (Torres et al., 2003; Vanneste et al., 2013; Han et al., 2014; Feng and Chen, 2015). Previous studies showed that Fe-Mn nodules in the SCS were mainly hydrogenetic deposits (Lin et al., 2003). However, little work on genetic models for nodule and crust growth in the different oceanographic and geotectonic settings in this area has been undertaken.

Based on mineralogy, composition, source of fluids and tectonic settings, sedimentary Fe-Mn oxides are classified as hydrogenetic, diagenetic, hydrothermal and mixed-type deposits (Bolton et al., 1988; Hein et al., 1997). Traditionally, the genesis of oceanic nodules and crusts can be discriminated by using the ternary diagram $\text{Mn-Fe-(Cu + Ni + Co)} \times 10$ (Bonatti et al., 1972). Mn/Fe ratios for other deep-sea polymetallic nodules are different compared to shallow water continental margin nodules from other ocean basins and nodules and crusts from the northern SCS from this and previous studies (Fig. 11 and Supplement Table A3). However, this approach cannot be used to clearly distinguish between hydrothermal and diagenetic precipitates. The REY pattern can be used to differentiate between hydrothermal Mn and Fe deposits, diagenetic Fe-Mn nodules, and hydrogenetic Fe-Mn nodules and crusts (Bau et al., 2014).

Compared with typical oceanic hydrogenetic-diagenetic nodules from the Indian Ocean (Mukhopadhyay et al., 2003) and CCFZ (Wegorzewski and Kuhn, 2014), most of the nodules and crusts from the northern SCS plot in the hydrogenetic or mixed hydrogenetic-hydrothermal fields on this ternary diagram (Fig. 11). The NESCS Fe-rich nodules contain redox-sensitive minerals (such as pyrite) (Fig. 6a), reflecting mineralization fronts associated with redox boundaries in the sediment column during early diagenesis, as also occur in Fe-Mn nodules from the Gulf of Cadiz (González et al., 2012). Furthermore, most NESCS nodules exhibit Mn/Fe values <0.25 and low contents of Co, Ni, Cu and REEs (Table 2), and plot near the Fe end member (Fig. 11a). There are many studies documenting nodules from shallow waters and con-

Fig. 11. Ternary diagram for ferromanganese genetic models adapted from Bonatti et al. (1972). All data plotted as wt.%. (a) Comparison of different areas of Fe-Mn nodules from the northern SCS. The fields are: (A) NESCS, (B) NWSCS, (C) CBSCS; (b) Comparison with other deep-seabed Fe-Mn nodules and continental margin nodules. Selected literature data from marginal sea: Black Sea (Baturin et al., 2002), Gulf of Cadiz (González et al., 2009), East China Sea (Shan, 1984), Western Philippine Sea (He, 1991; Xu et al., 2006), California margin (Conrad et al., in press). Ocean basins: NW Pacific (Hein et al., 2012), Indian Ocean (Chandnani et al., 2012) and Clarion-Clipperton Fracture Zone (CCFZ) (Wegorzewski and Kuhn, 2014).

tinental margins where Fe, Mn and trace metal contents are similar to the nodules from the NESCS (Glasby et al., 1997; Baturin et al., 2002; González et al., 2009). All of those deposits display very low Mn/Fe ratios as a result of growth by predominantly diagenetic processes. In addition, the content of some elements in the nodules from the NESCS (V, Ca, Mg, Ni, Co, Mo) are more similar to shallow-water nodules from the Black Sea (Baturin et al., 2002), Gulf of Cadiz (González et al., 2007) and East China Sea (Shan, 1984) than to deep-sea nodules (Hein and Koschinsky, 2013). Co concentrations (up to 0.06 wt.%) and a slight positive Ce anomaly in some nodules from the NESCS (Fig. 10a) indicate exposure to bottom waters and hydrogenetic growth. The continental-margin-type nodules show lower total Co + Cu + Ni content and higher Fe, Al, and Cr concentrations than open-ocean nodules, reflecting the higher terrigenous input per unit area into the SCS (Koschinsky and Halbach, 1995; Hein et al., 2010).

On bivariate diagram of Ce_{SN}/Ce_{SN}^* versus Nd concentration (Fig. 12a), the Fe-rich nodules lack Ce anomalies and Nd concentrations are low (5–60 $\mu\text{g/g}$). In the bivariate diagram of Ce_{SN}/Ce_{SN}^* versus Y_{SN}/Ho_{SN} ratio (Fig. 12b), the Fe-rich nodules show slight negative Y and Ce anomalies. Both diagrams discriminate these nodules as diagenetic in origin, but overlaps slightly with the hydrothermal field. Negative Ce anomalies have also been found in a number of hydrothermal Fe-Si-oxyhydroxides (Fig. 10e) and have precipitated from a fluid composed primarily of ambient seawater with little hydrothermal fluid (Dekov et al., 2007). Alternatively, negative Ce anomalies in seep carbonates suggest that they may result from high porewater alkalinity in the presence of organic matter (Fig. 10d). In addition, the average GR of the NESCS nodules (3320 mm/Myr) is slower than those calculated for shallow-water Baltic Sea nodules (average rate is 20,000 mm/Myr) (Zhamoïda et al., 1996; Hlawatsch et al., 2002), but several

Fig. 12. Marine Fe-Mn oxyhydroxide deposits for (a) Ce_{SN}/Ce_{SN}^* vs Nd concentration; (b) Ce_{SN}/Ce_{SN}^* ratio vs Y_{SN}/Ho_{SN} (Bau et al., 2014); SN is shale normalized to Post-Archean Australian Shale, PAAS (McLennan, 1989).

orders of magnitude higher than GRs of hydrogenetic NWSCS and CBSCS nodules (from 4 to 7 mm/Myr). Therefore, fast growth rates emphasize the importance of sediment diagenetic processes (Reyss et al., 1982). Furthermore, this relatively rapid accretion in a short span time is probably one of the main causes for the overall low content of transition metals other than Fe and REE in these continental margin nodules.

The Fe-Mn nodule samples in the NWSCS result in Mn/Fe values between 0.54 and 1.25 with a mean of 0.89, which is consistent with a predominantly hydrogenetic origin for these continental-margin Fe-Mn nodules and crusts. They are similar to other samples from the western Philippine Sea (He, 1991; Xu et al., 2006) and, California continental-margin (Conrad et al., in press), and are more enriched in Fe than the crusts from the Pacific Ocean (Hein et al., 2012). In addition, these nodules show high contents of Ti and REE and strong positive Ce anomalies, characteristic of a hydrogenetic origin. Most samples plot outside of the typical open-ocean hydrogenetic field, but within the field typical for Pacific continental-margin and small ocean basin Fe-Mn crusts (Hein et al., 2000). Data that plot in the transition between the diagenetic and hydrogenetic end members indicate participation by both processes in nodule formation (Fig. 11b). Fe-Mn nodules and crusts from the CBSCS plot in and near the typical open-ocean hydrogenetic field and are similar to deep-sea nodules from the northwest Pacific (Hein et al., 2012) (Fig. 11b). Nodule J-158 from the CBSCS contains relatively low Co (0.12 wt.%) and high Cu and Ni, probably indicating a predominance of diagenetically produced metals, with less hydrogenetic input. Plots of the NWSCS and CBSCS Fe-Mn nodules and crusts REY data normalized to PAAS are consistent with typical hydrogenetic Fe-Mn crusts plots (McLennan, 1989; Bau

et al., 2014) (Fig. 12). This characteristic hydrogenetic pattern shows a large positive Ce and negative Y anomalies, with some samples showing smaller positive anomalies for Eu, La, and Gd (Bau et al., 1996). Patterns from NWSCS and CBSCS Fe-Mn nodules and crusts samples show REY data generally consistent with hydrogenetic Fe-Mn crust patterns; two samples from stations S-9 and S-10 show less REY enrichment relative to PAAS, similar to mixed origin Fe-Mn nodules. Those crusts, might have had a diagenetic input from redox cycling in sediment from a nearby seamount.

5.3. Metal sources for Fe-Mn nodule and crust formation

The field sites, morphological characteristics, mineralogical and geochemical data from this study were compared with other deep seafloor Fe-Mn nodules and crusts, and shallow-water and continental-margin nodules from other ocean basins and tectonic settings. The substrate materials for northern SCS nodules and crusts are complex and include consolidated sediment (silicates, siliceous clay, silty clay and siliceous soft mud) (Luo et al., 1994) and basalt (Yan et al., 2015). There has also been controversy about the metal sources for the Fe-Mn nodules and crusts, with proposed sources including terrestrial weathering, submarine volcanic activity and seawater (Wang et al., 1986; Bao and Li, 1993; Lin et al., 2003).

To better understand the different genetic processes and metal sources for the northern SCS nodules and crusts, analytical data of Fe-Mn nodules and crusts from 28 different locations are used in a comparative study of latitudinal and longitudinal control on geochemical variation of samples (Supplement Table A3, Fig. 13). Ear-

Fig. 13. Chemical variation of northern SCS nodules: (a) Fe content (wt.%); (b) Mn content (wt.%); (c) Ti contents (wt.%); (d) Mn/Fe ratios. Large arrows with numbers represent annual sediment loading of surrounding major sources (unit: Mt/a, from Milliman and Farnsworth (2011)). The purple solid arrows are the pathways for the intrusion of the Northern Pacific Deep Water into SCS via the Bashi Channel/the Luzon Strait (Lüdmann et al., 2005; Gong et al., 2012); The orange arrows represent the assumed deep-water current circulation pathways in the northern SCS (Shao et al., 2007; Wang et al., 2010; Zheng and Yan, 2012). Black star represents mud volcanoes in the northern SCS. Black triangle represents Cenozoic basalts and volcanic rocks (Yan et al., 2008). The spreading axes are white double lines. There are three fossil spreading centers: the first one is oriented E-W in the northwest (NW) sub-basin; the second one is oriented E-W in the east sub-basin (near the present 17°N); and the third one is also in the east sub-basin (15.5°N) but extends southwestward into the southwest (SW) sub-basin. Data are from Briaes et al. (1993). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lier studies reported higher concentrations of Mn, Ni and Cu in nodules from siliceous sediments from the Central Indian Ocean Basin, indicating the influence of early diagenesis of organic matter in the sediments. In contrast, higher Fe and Co contents in nodules from pelagic red clay deposits are a result of greater hydrogenetic precipitation (Rao, 1987; Jauhari, 1989; Sudhakar, 1989). In the Marmara Basin of the Black Sea, high Mn concentrations are related to volcanic activity along fault planes (Ergin, 1994). Manganese is influenced by these processes and reduced Mn is remobilized from diagenetic reactions in shelf sediments. Unlike Fe, Mn in northern SCS nodules and crusts does not show a concentration increase towards the continental shelf. Manganese does show a negative correlation with increasing water depth as expected since dissolved Mn is enriched in seawater in the OMZ. Mn concentrations in Fe-Mn crusts are controlled by the redox potential of seawater from which the crusts formed. In the CBSCS, Mn/Fe values vary from 0.95 to 2.04, reflecting their open-ocean-type hydrogenesis, with possibly a minor diagenetic input (Fig. 13d). The todorokite and birnessite present in CBSCS nodules could be interpreted to indicate a suboxic diagenetic input and for crusts suboxic bottom water conditions. It is more likely that lower oxidation potential seawater conditions under which CBSCS deposits formed allowed for the precipitation of these Mn minerals that are less oxidant than δ -MnO₂, the mineral that typifies open-ocean crusts (Conrad et al., in press).

Moreover, along 18°N, Fe-Mn nodules and crusts show higher Mn concentrations and higher Mn/Fe compared with the NESCS, where the Fe content is highest. The chemistry of CBSCS nodules and crusts from the central deep basins located between the seamount chains is probably related to major fracture zones (e.g., Zhongnan Faults Zone) (Figs. 2b and 13b and d). Most of these seamounts in Province C are thought to have been emplaced after seafloor spreading stopped about 15 Ma ago. K-Ar and ⁴⁰Ar-³⁹Ar ages of dredged samples from seamounts as well as volcanoclastic records are all younger than 15 Ma (Wang et al., 1985; Kudrass et al., 1986; Yan et al., 2008), the estimated cessation age of seafloor spreading in the SCS. Especially, the Sc concentration in Fe-Mn nodules (Sc = 13 µg/g) and volcanoclastic rocks (Sc = 20 µg/g; Yan et al., 2008) in the CBSCS are similar and higher than that in the slope area (Sc = 9.7 µg/g). Sc is enriched in upper mantle and lower continental crust rocks, which suggests that the detrital fraction of the Fe-Mn nodules and crusts derives from the seafloor sediment and volcanic material (Ma et al., 1987). However, based on mass balance considerations, most of the Sc in the nodules must be sorbed, most likely on the Fe oxyhydroxide (Koschinsky and Hein, 2003). Similarly, the high Li content (64 µg/g) observed in nodule J-158 and moderate-to-high Mo, V and Pb concentrations could be related to volcanic-hydrothermal activity (Chan and Hein, 2007). Alternatively, the high Li contents in nodules are commonly of diagenetic origin, derived for redox reactions in the sediment (Hein and Koschinsky, 2013). As a result, these nodules and crusts act as a sink for metals dissolved in seawater in the CBSCS from the late Cenozoic to the present.

The NWSCS supports mostly smooth Fe-Mn nodules, which are essentially hydrogenetic with minor diagenetic input, and likely affected by a CDS. Terrestrial sources deliver trace metals to the surface ocean, specifically fluvial particulate matter delivered during winter precipitation is a significant source of Fe, Mn and other trace metals to the continental shelf (Liu et al., 2008). Eolian sources also contribute to the trace metal budget of the surface ocean (Chung et al., 2004). The strong positive Ce anomalies and high Ti (up to 1.57 wt.%) and Co (up to 0.23 wt.%) contents reflect water-mass dissolved metal composition and terrigenous input. Most of these nodules are located from 1000 to 2500 m water depth within or just below the oxygen minimum zone that promotes the enrichment in Mn, P, Co and other metals. Furthermore,

Ba and P both have nutrient-type profiles in seawater and can be used as a tracer of primary productivity (Chan et al., 1976; Broecker et al., 1982; Paytan and Griffith, 2007). They are also enriched in the NWSCS Fe-Mn nodules and crusts relative to open-ocean crusts. With the exception of a few outliers, P shows higher concentrations in near shore Fe-Mn deposits relative to off shore samples, which probably reflects the strong upwelling and primary productivity.

The SCS continental margin, especially in the NESCS, should promote the mobilization of Fe through redox reactions in the sediment and transport of dissolved Fe to the deeper areas (Conrad et al., in press; Fig. 13a), as in the Gulf of Cadiz (González et al., 2012). Fe-Mn oxide nodules from the Gulf of Cadiz have been described to occur in carbonate mud mounds related to fluid venting and also suggested to be strongly influenced by the Mediterranean Outflow Water (González et al., 2007). But in the NESCS, seepage activity gives rise to a variety of seafloor features including mud volcanoes and diapirs, pockmarks, brine pools and authigenic deposits of carbonates and barite (Figs. 2 and 13) (Chen et al., 2005; Han et al., 2014; Feng et al., 2015). This indicates that there is hydrocarbon-rich fluid flow originating at depth in the sediments in the NESCS, similar to the Gulf of Cadiz (Somoza et al., 2003; González et al., 2009; Medialdea et al., 2009). The genesis of Cadiz Gulf nodules and the NESCS Fe-rich nodules, originally composed of authigenic barite-pyrite and some pyrite-phosphate concretions, are associated with methane seeps that can aid in understanding fluid flow and sedimentary redox processes. The main source of Ba for the formation of authigenic barite in marine sediments is generally considered to be the dissolution of biogenic barite in sulphate-depleted porewaters (Brumsack, 1989; Torres et al., 1996). In this way, the precipitation of pyrite occurs by microbially produced HS⁻ reaction with iron from the sediments. Barite precipitation, on the other hand, takes place within the sediments through mixing of barium-rich, reduced seep fluids with pore water containing sulphate ion that is residual from microbial reduction in a semi-closed system (Canet et al., 2013). Furthermore, the lowest Mn/Fe and Ti concentrations are found for small Fe-rich nodules, suggesting formation within suboxic sediment during early diagenesis or on the seabed with minor hydrogenetic input (Fig. 13d). Ti is acquired primarily through sorption onto the Fe oxyhydroxide (Koschinsky and Hein, 2003), so its low concentration is related to the rapid growth of the nodules, which did not allow time for significant sorption to occur. This hydrocarbon flow promoted fluid migration (methane and metallic ions) and complexes with the metal ions in the sediment, together commonly through sulphate-reducing bacteria mediation (González et al., 2012).

6. Conclusions

In this paper, by combining new data and previous data for the northern SCS, we synthesize the mineralogical-geochemical data of Fe-Mn deposits over the entire northern SCS. The mineral deposits include three types: (1) Fe-rich nodules containing essentially goethite from the NESCS, with Mn/Fe < 0.25, low contents of Co, Ni, Cu in all samples, and very high estimated growth rates (up to 17,000 mm/Myr) indicating that diagenetic processes are predominant. The diagenetic processes are related to the deep-seated hydrocarbon production and circulation resulting in seafloor seeps probably partially through microbially-mediated anaerobic oxidation, similar to the Gulf of Cadiz; (2) Smooth Fe-Mn nodules and crusts essentially composed of asbolane, todorokite and CFA in the NWSCS have similar Fe and Mn contents (Mn/Fe = 1.19) and moderate trace metal enrichments, which is consistent with a predominantly hydrogenetic origin of continental mar-

gin Fe–Mn crusts; (3) Fe–Mn nodules and crusts composed of todorokite, asbolane, and birnessite in the CBCS with higher Mn and lower Fe contents (Mn/Fe = 1.42) than NESCS and NWSCS samples, which plot in the typical open-ocean hydrogenetic field on discrimination diagrams.

A number of factors may have influenced the formation of Fe–Mn nodules and crusts, especially their close proximity to terrestrial sources of dissolve and particulate material transported to the ocean, remobilization of Fe and Mn from sediment on the continental shelf and slope, upwelling and high primary productivity for high contents of Ba and P observed in nodules and crusts, and deep-water masses along the continental margin enriched in elements with long residence time. The concentration and distribution of Fe, Mn, Ti and Mn/Fe in nodules and crusts from the northern SCS show geographic variation. The NESCS shows the lowest Mn/Fe where small Fe-rich nodules occur, probably indicating a combination of early diagenetic, probably subsurface, formation with minor hydrogenetic input. They are derived from the oxidation of pyrite and pyrite-barite concretions, which are in related with redox boundaries and the methane-sulphate transition zone in the sediment. Iron is higher in NWSCS Fe–Mn nodules and crusts than in those from the open ocean, resulting in a higher Fe/Mn ratio. The Fe enrichment is due to redox cycling in continental shelf and slope sediment. The NWSCS deposits show increasing Fe concentrations with proximity to the continental shelf. The Ba and P are the elements associated with primary productivity and are enriched in the NWSCS deposits. The NWSCS supports mostly Fe–Mn smooth nodules that are essentially hydrogenetic with possibly a minor diagenetic input, and were likely affected by a CDS. However, CBCS nodules and crusts from the central deep basins located between the seamount chains, enriched in Sc and Li, are hydrogenetic and spatially related to the major fracture zone and associated volcanic-hydrothermal activity.

Acknowledgements

We are grateful to Prof. Dong Feng for their guidance and constructive discussions and Xuebo Yin, Yao Guan for help with element and petrology analyses. We thank Editor-in-Chief Mei-Fu Zhou, Dr. J.N. Pattan and other anonymous reviewers for their suggestions that improved the manuscript. This work has been financially supported by the project of the Chinese National Science Foundation (contracts 41376057, 41676056, 41306047) and the Spanish project SUBVENT (CGL2012-39524-C02). This study was benefited from the scientific cooperation between the South China Sea Institute of Oceanology and the Geological Survey of Spain (IGME).

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