Evidence for biogenic processes during formation of ferromanganese crusts from the Pacific Ocean: Implications of biologically induced mineralization

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ABSTRACT

Ferromanganese [Fe/Mn] crusts formed on basaltic seamounts, gain considerable economic importance due to their high content of Co, Ni, Cu, Zn and Pt. The deposits are predominantly found in the Pacific Ocean in depths of over 1000 m. They are formed in the mixing layer between the upper oxygen-minimum zone and the lower oxygen-rich bottom zone. At present an almost exclusive abiogenic origin of crust formation is considered. We present evidence that the upper layers of the crusts from the Magellan Seamount cluster are very rich in coccoliths/coccolithophores (calcareous phytoplankton) belonging to different taxa. Rarely intact skeletons of these unicellular algae are found, while most of them are disintegrated into their composing prisms or crystals. Studies on the chemical composition of crust samples by high resolution SEM combined with an electron probe microanalyzer (EPMA) revealed that they are built of distinct stacked piles of individual compartments. In the center of such piles Mn is the dominant element, while the rims of the piles are rich in Fe (MINERALIZATION aspect). The compartments contain coccospheres usually at the basal part. Energy dispersive X-ray spectroscopy (EDX) analyses showed that those coccospheres contain, as expected, $CaCO_3$ but also Mn-oxide. Detailed analysis displayed on the surface of the coccolithophores a high level of $CaCO_3$ while the concentration of Mn-oxide is relatively small. With increasing distance from the coccolithophores the concentration of Mn-oxide increases on the expense of residual $CaCO_3$. We conclude that coccoliths/coccolithophores are crucial for the seed/nucleation phase of crust formation (BIOMINERALIZATION aspect). Subsequently, after the biologically induced mineralization phase Mn-oxide deposition proceeds "auto"catalytically.

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1. Introduction

Ferromanganese crusts (Fe/Mn crusts) on seamounts are rich solid resources in the ocean, besides for manganese (Mn) also for cobalt (Co), tellurium (Te), thallium (Tl) as well as for platinum (Pt), rhodium (Rh) and iridium (Ir). These solid minerals (Clark et al., 1985; Baturin, 1993, 2007) have lately gained increasing economic value. Fe/Mn crusts have formed on seamounts, ridges and plateaus especially throughout the Pacific (Hein et al., 2000). They develop(ed) in water depths between 400 and 4000 m, with the thickest deposits in depths of 800–2500 m. In contrast to Fe/Mn nodules, which have been grouped according to their growth etiology into hydrogenetic and diagenetic nodules, crusts have only a hydrogenetic history (Halbach, 1986). Hence, the elemental composition of the crusts reflects the relative composition of the seawater rather than that of the sediment (Quinby-Hunt and Turekian, 1983). As taken from determinations of U-series or of Be radioisotopes the hydrogenetic Fe/Mn crusts grow slowly, with rates of about 1 to 10 mm/Myr (see: Hein et al., 2000). In turn, the ages of some crusts had been estimated to be about 70 Ma and can be dated back to the late Cretaceous (Klemm et al., 2005). The older, basal parts of crusts especially of thick crusts, are phosphatized, due to global phosphogenic events during the Tertiary (see: Glasby, 2006; Wang et al., 2008).

The general view is that crust formation is driven by hydrogenetic precipitations that are based on thermodynamic, surface-chemical and colloidal-chemical processes. This assumption is corroborated by bulk analyses revealing that almost all hydrogenetic elements identified in the crusts are found also in the seawater, and exist there as inorganic complexes (Halbach, 1986; Koschinsky and Halbach, 1995). As proposed the negatively

charged Mn-oxyhydroxides attract hydrated cations, while the more slightly positively charged Fe-hydroxides complex anions form larger complexes with low charge-density colloids (reviewed in: Hein et al., 2000). During the formation of Mn-oxyhydroxides, Mn(II) undergoes oxidation to Mn(IV).

Following the hydrogenetic precipitation hypothesis the colloids of Fe and Mn oxides, together with their adsorbed metal ions, precipitate on the hard-rock surfaces, under formation of poorly crystalline or even amorphous oxyhydroxides. This precipitation may be facilitated or even mediated by catalytic processes through bacteria (Hein et al., 2000). Hence a biomineralization component has been assumed to flank the mineralization processes. Until now no experimental data on the contribution of bacteria during the initial crust formation have been presented. However, well preserved eukaryotic microfossils have been detected in crusts. Those fossils include primarily calcareous coccoliths [Schumann Seamount] (Cowen et al., 1993) and foraminifera [Magellan Seamount cluster] (Glasby et al., 2007); the coccolith microfossils have been dated back to the Eocene [50 Ma] (Cowen et al., 1993).

The hydrogenetic crusts are found in the mixing layer between the upper oxygen-minimum zone [OMZ] and the lower oxygen-rich bottom zone [ORZ] (Koschinsky and Halbach, 1995; Koschinsky et al., 1997). The oxygen-rich bottom zone originates as Antarctic Bottom Water and contains mainly the oxidized forms of Mn, while in the upper oxygen-minimum zone reduced Mn(II) species are enriched (Koschinsky and Halbach, 1995). In turn it had been proposed that between the OMZ and the ORZ a massive precipitation of Mn due to oxidation processes, in form of Mn(III) and Mn(IV), takes place (Koschinsky and Halbach, 1995).

In the last years increasing evidence has been presented indicating that in nature some processes of mineralization are induced or controlled by organisms, or even enzymatically mediated (Lowenstam and Weiner, 1989; Weiner and Dove, 2003). Very recently first data on the participation of organic templates, matrices, on the formation of marine minerals, such as polymetallic nodules and crusts, have been presented (Wang and Müller, in press). It is proposed that especially during the formation of seed particles, required for the initiation of mineralization [nucleation of the floating, colloidal particles to gravitation-prone, falling particles], as well as during the attachment of those particles to an inorganic mineral template, living or dead organisms play a crucial role (Wang and Müller, in press; Wang et al., in press).

For the studies described here we used crust samples collected from the Magellan seamounts. The upper layer of the samples was taken to ensure that the mineral formation occurred fairly recently, and not during a subaerial episode (Wang and Wang, 1998, 1999; Wang et al., 1998; Glasby et al., 2007). We report on the presence of large assemblages of coccoliths/coccolithophores in those crust samples. Since those unicellular algae live and proliferate in the upper, photic zone down to ≈100 m (Hay, 2004), it must be supposed that they fell down from the ocean surface to the mixing layer between the OMZ and the ORZ and underwent there mineral transition/transformation from Ca-carbonate to Mn-oxide. Our data also suggest that coccoliths are the driving factors for the oxidation of Mn(II) during the transition of $CaCO_3$ to MnO_2 (by acting as bio-seeds). Hence we propose that crust formation is the result also of biomineralization processes.

2. Materials and methods

2.1. Ferromanganese crust

The ferromanganese crusts (labeled RZO7) had been collected from a depth of 2250 m by the research vessel "Ocean 1" from Magellan seamounts in the western Pacific Ocean in 2002.

2.2. Element composition of the crust

The element composition of the crust was determined by the method described by Wang et al. (2000). The concentrations of Mn, Fe, Co, Ni, Cu and P in the ferromanganese crust were determined by the Panalytical Axios X-ray spectrometer. The samples were ground to homogeneous powder of about 200 mesh in an agate mortar, and directly compressed to powder pellets for the determination. The absorption-enhancement effects between the elements were corrected by theoretical α-coefficients. The calibration was finished by using the certified reference materials of ferromanganese nodules and crusts (Wang et al., 1998, 2003). Our study samples originate from the surface area (depth 4 mm) of the crust. These regions are low in phosphorus (<2%), indicating that they are from non-phosphatized crust layers.

2.3. Digital light microscopy

The analyses were performed with a VHX-600 Digital Microscope from KEYENCE (Neu-Isenburg, Germany), equipped with a VH-Z25 zoom lens [magnification from 25× to 175×] or a VH-Z50 long-distance high-performance zoom lens [with a magnification of up to 500×]. This set-up allowed also in depth visualizations and 3D reconstructions have been carried out.

2.4. Electron microscopy

High resolution scanning electron microscopy (HR-SEM) was employed to study the morphology of the crusts. For this purpose cleaned parts were mounted onto aluminum stubs (SEM-Stubs G031Z; Plano, Wetzlar, Germany). Subsequently, electron microscopic inspection was performed with a Gemini Leo 1530 high resolution field emission scanning electron microscope (Oberkochen, Germany).

2.5. Electron probe microanalyzer (EPMA)

Selected sections from the crust were investigated by electron probe microanalyzer (EPMA); the surfaces were polished with diamond paper. Prior to analysis these samples were coated with a 100 Å-thick layer of carbon and finally inspected by EPMA connected to a wave dispersive spectrometry system, using a JEOL 8200 Instrument. The operating conditions of the electron microprobe were 20 kV accelerating voltage, 20 nA current, and a spot size of 5 μm. EPMA was used for spot analysis to obtain quantitative results as well as for scanning analysis to get elemental maps for μm² to mm² level areas.

2.6. Spectroscopy: EDX and EDX mapping

Energy dispersive X-ray spectroscopy (EDX) was performed with an EDAX Genesis EDX System attached to a scanning electron microscope (Nova 600 Nanolab; FEI, Eindhoven; The Netherlands) operating at 15 kV with a collection time of 30 s. Areas of approximately 20 μm² were analyzed.

The X-ray maps (EDX maps) were obtained as follows: samples were positioned 5 mm below the objective lens of the SEM (Nova 600) operating at 10 kV and tilted by 52° resulting in a perpendicular incidence towards the X-ray beam. Elemental distribution (mapping) of the crust samples was qualitatively assessed by an energy dispersive X-ray spectrometer from EDAX (EDAX Division, Wiesbaden, Germany) coupled to a focused ion beam (FIB) assisted SEM at an operating voltage of 15 kV and a beam current of approximately 3.0×10^{-9} Å. The analytical system was calibrated using an internal standard. The data were analyzed using the KEVEX Advanced Imaging software (KEVEX Corporation,