Intrusive contacts, porphyry dikes, hydrothermal breccias and mineralized veins, all show clear NNW and NE preferred orientations, indicating that pre-existing normal faults inherited from the extensional period channelled the ascent and emplacement of magma and hydrothermal fluids during the compressive stage. Statistically, there is an overwhelming predominance of NE and NNW-NW fault planes; N-trending faults, parallel to the orogen, are statistically insignificant and restricted to the eastern margin of the Abanico basin. The abundance of syn-tectonic hydrothermal minerals confirms that fault inversion occurred under high fluid pressures, as it can be inferred by the slip plane infilling of minerals such as epidote, chlorite, tourmaline, quartz, calcite and Cu-Fe sulphides. Given the high dip angle of the faults (60–0°), the compressive tectonic regime and the presence of hydrothermal fluids during faulting, the required conditions for reactivating severely disoriented faults, such as supralithostatic fluid pressures, are met [Sibson, 1985].

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TWO STEP MICROBIAL FORMATION MODEL OF BLACK SHALE-HOSTED MANGANESE CARBONATE DEPOSITS – CASE STUDY OF THE URKUT DEPOSIT, HUNGARY

Рассмотрено формирование низкотемпературных карбонатно-марганцевых месторождений, приуроченных к черносланцевым толщам, в окислительных условиях на стадии биогенного восстановления Mn^{3+} и Mn^{4+} при диагенезе. Приводятся данные о геологическом строении, минералогии и геохимии гигантского неметаморфизованного месторождения карбонатных марганцевых руд Уркут юрского возраста. Изотопный состав углерода карбонатов свидетельствует о его органогенном источнике, изотопный состав кислорода – о температурах

образования 17–23 °C. Источником металлов служили придонные гидротермальные флюиды, в результате деятельности которых формировались гидроксидно-марганцевые руды с преобладанием Mn^{3+}. Разнообразие оксидных минералов марганца в рудах объясняется с термодинамических позиций кислотно-основными свойствами растворов и наличием окислительно-восстановительного барьера. Бактериальное окисление органического углерода является необходимым условием для образования крупных залежей карбонатов марганца в черносланцевых толщах.

Introduction

To start any consideration concerning manganese we have to be aware of the sneaky (tricky) behavior of this element. Tracing the source of metals is very important, but enrichment effects, the way of accumulation of Mn (ore) are also important, and these two together let to propose a genetic picture.

The role of microorganisms in sedimentary and low temperature hydrothermal ore deposits is being increasingly appreciated, among them chemolithotrophs. Formation of black-shale hosted manganese-carbonate ores is an example of a low-temperature bacterial system characteristic of non-sulphidic, oxic environments.

Early diagenetic bacterially mediated Mn(IV) and Mn(III) reduction processes via organic matter oxidation and Mn-carbonate mineralization are well established [Polgari et al., 1991]. However, the fundamental processes of formation of these huge black-shale hosted accumulations of manganese was still poorly understood.

To address these issues, the well preserved, unmetamorphosed, black shale-hosted manganese-carbonate deposit of the Urkut Basin, Hungary offers an excellent case study for detailed petrographic, mineralogical, geochemical, and textural analyses. These early diagenetic Mn carbonates and primary Mn oxides are of Jurassic (Lias-Toarcian) age [Polgari et al. (eds.), 2000 and references therein]. This important deposit is among the 10 largest Mn deposits with current reserves of 80 million tons of Mn-carbonate ore (24 weight percent average Mn and 10 weight percent Fe).

Here, we review the main characteristics of the black shale-hosted Urkut Mn deposit, provide additional geochemical and geomicrobiological evidence for the chemolithoautothroph bacterial activity as a fundamental process of manganese-ore formation, discuss the importance of such deposits as paleoenvironmental indicators, provide a new general model for the origin of this type of deposits.

Geological setting and characteristics of the ore deposit at Urkut

The black shale-hosted Mn-carbonate ore bed is about 40 m thick. The ore deposit of economic importance now covers an area of 8 km^2. The ore deposit occurs in a limestone section and consists of three ore beds (10-, 3-, and 1 m thick), separated by a 20- and 4 m-thick black shale. The rhodochrosite ore is composed of laminated, alternating grey, green, brown, and black sections composed of mixtures of very fine-grained (1–2 µm) carbonate minerals and clay [Polgari et al., 2000].

The bulk XRD mineralogical composition of the Mn-carbonate ore beds shows rhodochrosite (Ca-, Mg-bearing), siderite, kutnohorite, 10A-phyllosilicate (celadonite), smectite (nontronite), goethite, quartz, Ca-apatite (phosphorite), and pyrite, with traces of chlorite, zeolite, feldspar, and manganite. The host black-shale consists of quartz, calcite, pyrite, smectite, 10A-phyllosilicate (illite, celadonite), goethite, and chlorite, with traces of zeolite, and feldspar. Manganite is the only Mn-oxide phase in the carbonate ore bed.

Mn-carbonate ore samples have average $\delta^{13}C$ value –16.8 ‰ PDB. These values reflect a significant input to the carbon reservoir from which the $MnCO_3$ formed from the degradation of organic matter via bacterially mediated early diagenetic processes [Polgari et al., 1991, second microbial cycle]. The $\delta^{18}O$ isotope values vary between –5.84 and +1.61 ‰ PDB, which reflect temperatures of precipitation between 17 and 23°C [Polgari et al., 2012].

Biomineralization – general aspect

Microbial geochemistry the development of research methods has allowed investigations of extant biogeochemical systems, which has produced considerable new insights into bacterially mediated Mn mineralization [Mandernack and Tebo, 1993; Mandernack et al., 1995; Moffett and Ho, 1996; Bargar et al., 2005; Webb et al., 2005]. Morgan [2005] provided a thermodynamic analysis of microbial Mn(II) oxidation in low temperature aquatic systems, giving a kinetic model of oxidation pathways for

Mn(II). Bacterial oxidation of Mn(II) to Mn(IV) is thought to drive the oxidative segment of the global biogeochemical Mn cycle [Krumbein, 1983; Ehrlich, 1990]. This important redox system is believed to be driven by an enzyme or enzyme complex involving a multicopper oxidase [Tebo et al., 1997].

Proximal environment

At Urkut-Csardahegy, a large Fe-Mn-oxide chimney system containing fluid-flow microchannels characterized the basin. Stromatolitic mounds grew at the sediment/water interface, which buried the chimneys. These prove the local hydrothermal metal source for mineralization. [Polgari et al., 2012].

Distal environment

It is difficult to decipher the original aerobic microbial cycle because the whole deposit was overprinted by anaerobic heterotrroph secondary microbial processes. But some remnants produced during the original processes are preserved in the Urkut Mn carbonate deposit, among which most importantly is the presence of manganite (MnO(OH)). To understand this so-called long-standing mineral phase, a detailed explanation is needed. During development of the Mn-oxide proto-ore, the first product of microbial Mn(II) oxidation probably was a bio-oxide based on the experimental studies of Villalobos et al. [2003], Bodeï et al. [2007], and others. This bio-oxide is an X-ray amorphous oxide similar to δ-MnO_2, which is thought to be a disordered thermodynamically unstable 7Å-vernadite (hexagonal phyllomanganate) containing Mn(IV) vacancy defects, having very small particle size (< 20 nm lateral dimensions), and having only two or three MnO_2 layers (Mn is in octahedral coordination) stacked along the c axis [Villalobos et al., 2003]. A structural model for the initial amorphous bio-oxides indicates that bacterial processes oxidize Mn(III) to (IV) via an enzymatic pathway [Bargar et al., 2005]. Based on the their results, it is assumed that Mn(IV) polymerization leads to sheet polymers or nanoparticles with a general structural formula of $Mn_xO_2^{(4x-4)}$ (x ≤ 1) that exhibit the basic hexagonal phyllomanganate structure, but contain numerous vacancy defects and other structural defects [Bargar et al., 2005]. Reaction of Mn(II) with the primary biogenic oxide results in the production of abiotic secondary products, feitknechtite or a 10A Na-phyllomanganate [Bargar et al., 2005]. The identity of the secondary product depends upon the Mn(II) concentration as described by thermodynamic relations [Mandernack et al., 1995]. A decrease in the dissolved Mn(II) appears to act as a reductant for the biogenic oxide and to control the stability of secondary abiotic reaction products. The stability of Mn(III)-bearing phases such as MnO(OH) and Mn_3O_4 increases relative to that of Mn(IV)-bearing phases such as MnO_2 as pH and Mn(II) concentration increase. This behaviour can be seen from the reaction for MnO(OH) transformation to MnO_2 in aqueous solution: $2H^+ + 2MnO(OH) = MnO_2 + Mn^{2+} + 2H_2O$.

In ancient Mn-ore beds manganite is the common Mn(III) oxide phase and it is widely thought to reflect oxygen-deficient conditions [Roy, 1981]. Taking into consideration recent research, the existence of manganite may reflect high Mn(II) concentrations rather than an indicator of a suboxic environment. Giovanoli R. [1980] reported that the rate-determining step in γ-MnO(OH) (manganite) formation is the transformation of the rapidly formed initial products, such as feitnechtite, to manganite.

On the other hand, if the Mn(II) concentration is less than that in 7Å-vernadite, then 10Å (Na, Mg) phyllomanganate forms and during Mg^{2+} uptake Mg todorokite forms while the phyllomanganate transforms to tectomanganate. Interlayer Mg serves as a template for the transformation of 10Å-vernadite to todorokite. The abundance of Mg in seawater and its key role in converting phyllomanganate to tectomanganate explain why todorokite is common in marine diagenetic and hydrothermal ferromanganese oxides [Bodeï et al., 2007], but does not explain its near absence in marine hydrogenous deposits. Experimental studies showed that extracellular polymers from bacteria catalyze the adsorption of Mg on the surface of the cells [Mandernack et al., 1995]. The Mg uptake can be responsible for the elevated Mg content in black shale-hosted Mn-carbonate deposits. So the bacterial cells not only directly oxidize Mn(II) to Mn(IV) but also, in the early stages of oxidation, influence the cation composition of the Mn-oxide mineral being produced. Later chemical processes start to obscure the biological signal [Tebo et al., 1988].

The high Mg content of the black shale-hosted Mn-carbonate deposits might provide a geochemical proxy for early-stage aerobic chemolithoautotroph processes in the formation of huge Mn deposits. Previous chemical investigations showed high Mg contents in black shale-hosted Mn-carbonate deposits from Urkut (2.5–8 wt. % MgO). High Mg contents were reported without any ex-

planation for similar Mn deposits from Molango, Mexico [Okita et al., 1988] and Chinese deposits [Hein and Fan, 1999].

Microbial evidences and their palaeoenvironmental interpretation

Black shale-hosted manganese deposits contain a huge mass of mineralized bacteria that are at least in part responsible for major accumulations of metals in sediments by sequestering them from hydrothermal sources and seawater. Positive Ce anomalies are further evidence of oxidic conditions.

Aerobic chemolithoautotroph microbial model

Marine Mn-bearing deposits are generally classified as three types: hydrogenetic, diagenetic, and hydrothermal [Bolton et al., 1988; Hein et al., 1997]. The first type is represented by ferromanganese crusts, which slowly precipitate from seawater at the seafloor on to hard-rock substrate. Diagenetic deposits result from direct precipitation of Mn during early diagenesis at/or below the seafloor, which is usually related to changing redox conditions, where Mn-rich sediments accumulate where oxygenated water mixes with oxygen-deficient water (bath-tub-ring redox-interface model) [Force and Cannon, 1988; Frakes and Bolton, 1992]. These diagenitic deposits may be composed of Mn carbonates or oxides. Manganese deposits related to submarine hydrothermal system belong to the third type. It is evident that formation of huge black shale-hosted Mn-carbonate deposits cannot be explained solely by these three deep-ocean processes. For diagenetic-type redox-interface models into which these depsosits are placed, additional mechanisms are required. Mn-carbonate formation took place via bacterially mediated Mn(IV, III) reduction through C_{org} oxidation, and not from direct precipitation as carbonates from seawater. Under these circumstances, ore-deposit formation was the primary process that resulted from Mn (III, IV) oxide proto-ore accumulation. Thus, a fourth type of genetic model is required for these deposits, that is a model in which an aerobic, chemolithoautotroph microbial cycle (cycle I) are followed by an anaerobic heterotroph bacterial cycle (cycle II).

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UPPER CRETACEOUS HYDROTHERMAL CHIMNEY FRAGMENTS FROM THE EASTERN PONTIDE BELT, NE TURKEY: IMPLICATIONS FOR PONTIDE VMS DEPOSITS

Изучены трубы «черных курильщиков», обнаруженные в колчеданных месторождениях позднемелового возраста в западной части Понтид. Присутствие минерализованных фрагментов труб в колчеданных месторождениях западной части Понтид и содержания рассеянных элементов в них представляют собой значимые данные для понимания физико-химических условий и истории отложения колчеданной минерализации на океаническом дне.

Introduction

The fossil hydrothermal chimney fragments which have been documented to date in the volcanogenic massive sulfide (VMS) districts are quite limited and specific to very few districts (Urals, Cyprus and Japan). The relics of paleo-sulfide chimney fragments were first described in the Kuroko type VMS deposits of Japan, by Scott [1981]. Later, well preserved paleo-sulfide chimneys were described in the VMS deposits in Urals [Herrington et al., 1998; Maslennikov, 1991, 1999, 2006], Cy-