Sedimentary Geology 296 (2013) 55–71

Contents lists available at ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo

Facies-related baryte mineralization bearing Cu–Zn sulfides in Miocene estuarine deposits of the upper Rhein Graben (Wetterau, Central Germany)

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ARTICLE INFO

Article history:
Received 26 March 2013
Received in revised form 5 August 2013
Accepted 7 August 2013
Available online 14 August 2013

Editor: J. Knight

Keywords:
Baryte
Hydrothermal
Estuary
Miocene
Central Germany

ABSTRACT

Baryte with or without base metal sulfides is quite common in sediments deposited in open marine environments or in continental sedimentary basins. Its precipitation is caused by hydrothermal processes, related to diagenesis, and frequently mediated by biogenic processes. The current study is focused on siliciclastic sandstones of Miocene (Aquitanian) age in an estuarine environment in the Wetterau region of the Rhein Graben, central Germany. In the estuarine environment only the central basin and the landward delta are host to a diagenetic and subsequent hydrothermal mineralization.

Diagenesis took place under near-ambient ($T \approx 25$ °C) conditions and resulted in strong pyritization ($-0.75 < Eh < +0.25$, $pH > 5$) in the central basin. Diagenesis is more landward represented by a pervasive silicification ($pH < 12$) in deltaic sandstones.

Epigenetic mineralization (100°–130 °C) with pyrite in the central basins was succeeded by Cu–Zn–(Sb) minerals ($0.75 < Eh < 0/5 < pH < 11$), silicification and kaolinization ($2 < pH < 9.5$) and eventually by the formation of gibbsite ($3 < pH < 8$). At the transition from the delta to the estuarine funnel, baryte is of very widespread occurrence. Its variegated texture and crystal morphology allow for a precise determination of the hydraulic system as marine phreatic, freshwater phreatic, and freshwater vadose. The narrow size of the rift graben and its sealing against the open sea fostered concentration of Ba and enhanced the redox processes. Hypogene brines along with Miocene volcanic activity provided the metals, and marine ingressions in this transitional environment supplied the sulfur. Sulfides were concentrated in the finer-grained rocks because of their enrichment in organic material, while sulfates accumulated in the more permeable coarser sandstones.

1. Introduction

Baryte [$BaSO_4$] has been recorded from a wide range of depositional environments, as cement in sandstones and filling centimeter-sized vugs and meter-sized caves in calcareous rocks (e.g., Carpenter and Fagan, 1969; Lynn et al., 1971; Large, 1981; Purvis, 1992; Gluyas et al., 1997; Dinelli et al., 1999; Bonny and Jones, 2008). In places, the baryte concentration may even achieve ore grade (Turner and Goodfellow, 1990; Maynard and Okita, 1991; Valenza et al., 2000; Clark et al., 2004; Kontak et al., 2006; Dill, 2010).

The Neogene Rockenberg Beds hosting the baryte mineralization are well exposed by extensive sand pitting about 40 km north of Frankfurt am Main (Frankfurt upon the River Main), in the environs of Rockenberg and Münzenberg (Fig. 1). In the current study, the sandstone-hosted baryte roses were investigated mineralogically and chemically (trace elements, isotope analyses) for the following reasons. The environment of deposition at the transition from land to sea is very uncommon for the mineralization of baryte in sedimentary rocks. Baryte precipitation is not the result of a series of sedimentary processes but also involves hydrothermal solutions being involved in the concentration of baryte. With this in mind, the depositional environment and the genetic processes are not only of interest to sedimentologists working in this field of study but it has also implications for applied sedimentology and economic geology, in particular. It adds up a new target area for baryte exploration. The mode of formation and depositional environment are described in detail from the sedimentological point of view and the physical–chemical regime (Eh, pH, temperature of formation) is going to be modeled thermo-dynamically.

2. Methodology

Field work comprised mapping of the sand pits and sampling of them along cross sections covering the walls and benches of sand pits

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http://dx.doi.org/10.1016/j.sedgeo.2013.08.003

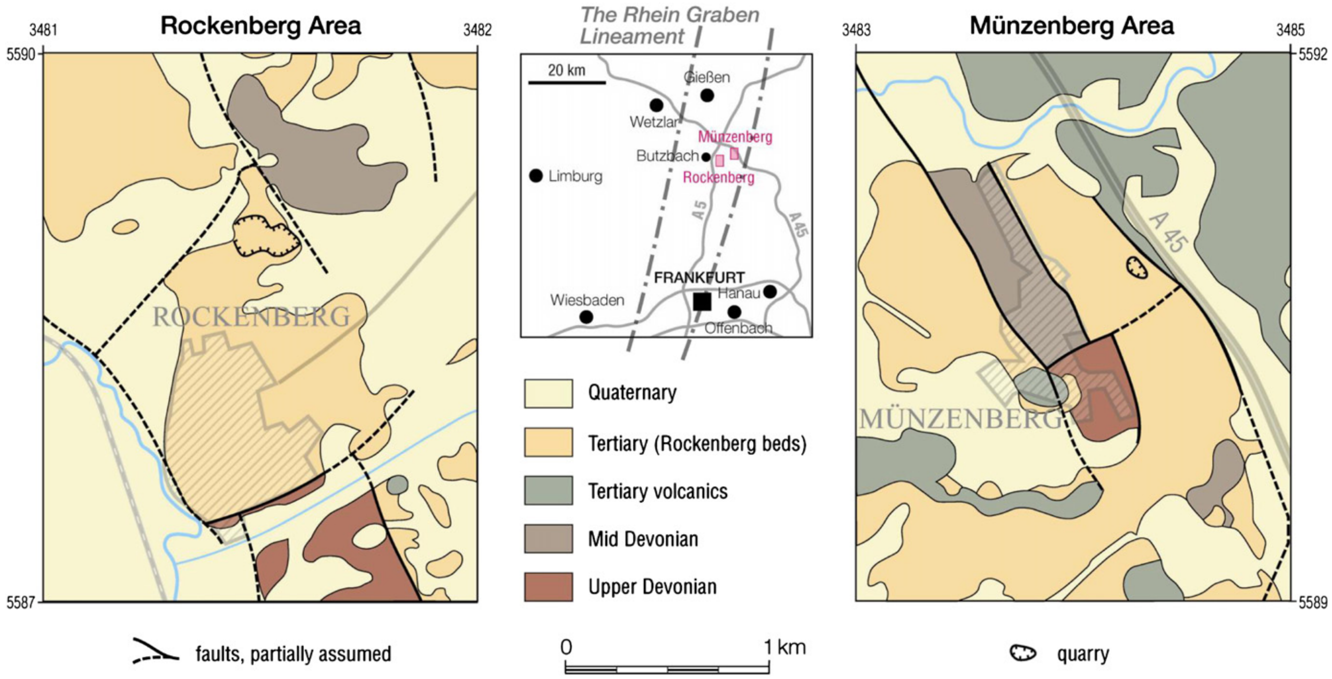

Fig. 1. The study area (red rectangles) about 40 km north of Frankfurt am Main in the environs of Rockenberg and Münzenberg. The Rockenberg Beds are representative of what has been denoted as Tertiary beds in both maps and in the legend.

in the region. The samples were split, with one half of the sample crushed for chemical analyses and the other one cut for mineralogical analyses. Laboratory-based investigations of 25 samples involved routine optical mineralogy supplemented by X-ray diffraction (XRD) and scanning electron microscopy. For XRD, a Philips diffractometer PW 3710 (40 kV, 30 mA) with CuKα radiation was used. The scanning electron microscope FEI QUANTA 600 FEG with an energy-dispersive system (SEM-EDS) was used to assist in mineral identification and for morphological studies. As some minerals could be better identified using their spectroscopic signature, infrared spectroscopy was carried out in addition to the routine XRD. For measuring mid-infrared spectra (MIR) the KBr pellet technique (1 mg sample/200 mg KBr) was applied. Spectra were collected on a Thermo Nicolet Nexus FTIR spectrometer (MIR beam splitter: KBr, detector DTGS TEC; FIR beam splitter: solid substrate, detector DTGS PE). The resolution was adjusted to 2 cm^{-1}. Spectra were recorded before and after drying of the pellets at 150 °C and vacuum. Only the spectra of the dried pellets are shown.

Major and trace elements were analyzed by X-ray fluorescence spectrometry (XRF) at BGR (Federal Institute for Geosciences and Natural Resources) in Hannover on powdered samples (PANalytical Axios and a PW2400 spectrometer). Samples were prepared by mixing with a flux material and melting into glass beads which were analyzed by wavelength dispersive XRF (WD-XRF). To determine the loss on ignition (LOI) 1000 mg of sample material was heated to 1030 °C for 10 min. After mixing the residue with 5.0 g lithium metaborate and 25 mg lithium bromide, the samples were fused at 1200 °C for 20 min.

The isotopic composition of sulfur and oxygen in the baryte roses was measured in continuous flow technique with an isotope ratio mass-spectrometer (Isoprime, GV Instruments, UK) coupled online with an element analyzer (EuroEA) in the Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, Germany. In this setup, sulfur is liberated as SO$_2$ by combusting the finely powdered BaSO$_4$ in the reactor column of the element analyzer in an oxygen enriched environment, whereas the isotopic composition of oxygen is measured as CO from the pyrolitic decomposition of sulfate at 1430 °C in a high-temperature oven (HEKAtech, Germany). After chromatographic separation of the gaseous combustion products, the species used for the isotope measurements (SO$_2$ and CO, respectively) were transported with a constant helium stream into the mass-spectrometer. The isotope ratios measured relative to a reference gas were calibrated by using the standard materials IAEA-S1, -S2, and NBS 127 for sulfur and NBS-19, NBS-127 and N3, for oxygen. Precision estimated based on the statistical spread of three independent measurements on each of the samples (one standard deviation) was better than 0.2‰ for sulfur and <0.3‰ for oxygen. Results are given on the V-SMOW and V-CDT scales for oxygen and sulfur, respectively.

3. Geological setting

During the Cenozoic the Wetterau region, Germany, formed part of the northern Upper Rhine Graben in the Alpine Foreland (Fig. 1). An outline of its paleogeography was given by Kuhlemann and Kempf (2002) and Sissingh (2003). An initial fluvio-lacustrine phase of sedimentation was followed by conglomeratic fans evolving at the graben margins. In the south of the rift basin, K-bearing salt units developed, whereas in the Mainz Basin fluvial to lacustrine basins persisted. This period is also characterized by an early Rupelian marine ingression from the North Sea. During the Late Oligocene and Early Miocene, the region called today the Wetterau became part of this rift basin and was affected by erosion, uplift, and continental sedimentation interrupted by a few brackish-marine ingressions. A continental environment prevailed, leading to large sand beds devoid of any calcareous sediments. The pervasive fracturing along with formation of the Rhein Graben provoked the ascent of basaltic lava during the Late Miocene (Kümmerle, 1981). The deposits have been extensively quarried in the environs of Rockenberg and Münzenberg about 40 km north of Frankfurt, Germany (Fig. 1). The Pb–Cu–Zn–Ba mineralization in vein-type deposits, karst cavities and lenses within and on top of the Rheinisches Schiefergebirge has been investigated by Schaeffer (1984).

4. Results

4.1. Lithology and paleontology

The entire Tertiary lithological series is cut by normal faults into a mosaic of more or less rectangular blocks of sandstones, the latter called