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In-situ analyses of carbonaceous matter in manganiferous black shales: Analytical proxies and implication for ore processing

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ABSTRACT

Carbonaceous matter is generally known to be problematic for metal recovery during metallurgical processing of black shales. In particularly, metal upgrading during beneficiation prior to (bio-) hydrometallurgical and/or pyrometallurgical processing is hindered by the presence of abundant carbonaceous matter (CM). This study presents the characterization of CM and mineral bound carbonaceous matter (CMP) in three manganese carbonate-rich shales hosting 6–8 wt% total organic carbon. Non-destructive methods, such as incident light microscopy, scanning electron (SEM) and focused-ion-beam-transmission electron microscopy (FIB-TEM), QEMSCAN and electron microprobe, were used to show that free CM is adsorbed onto illite-smectite surfaces. This form of CM ranges in grain size from sub-micrometer up to ≈100 µm. The most efficient method to show the illite-smectite association is SEM and for quantification of this association, QEMSCAN should be used. Mineral-bound carbonaceous matter may be relicts of extrapolymers (pyrite and/or carbonate) and needs characterization using FIB-TEM. The quantity of CM can then be estimated by a rough calculation as the difference between the total organic carbon (Rock Eval) and the free carbon calculated from normative mineral compositions based on X-ray Fluorescence (XRF) and X-ray-Diffraction (XRD) analyses. The mineral bound CM could not be detected by QEMSCAN under conventional analytical conditions. We estimated that about 85% of the CM in the test samples was adsorbed on mineral surfaces and about 15% was bound to minerals. The physical protection of the CM by clays, and the morphological and density differences between pyrite, carbonates and biochemically-bound CM in pyrite/carbonates needs to be taken into consideration in the process design.

1. Introduction

Adverse effects of naturally occurring carbonaceous matter on metallurgical processing, in particularly during flotation, is reported for Au, Cu, Pb and Zn ores hosted by black shales (Hausen et al., 1985; Abtosi and Osseo-Asare, 1986; Hutchins et al., 1988; Adams and Burger, 1998; Afenya, 1991; Pyke et al. 1999; Ofori-Sarpong et al., 2013).

Carbonaceous matter elimination from manganese carbonate-rich rocks through flotation is problematic because: (i) it adsorbs on the carbonate surfaces, (ii) it can be intergrown with carbonates as relict carbonaceous matter from a biomineralisation process (Orberger et al., 2007), or (iii) it can be formed during biomineralisation, as exopolymers e.g. (EPS; Sklodowska and Matlakowska, 1998).

The prediction of the behavior of CM during processing, such as flotation, is complicated because of the small grain size of the material, the high ad/absorption capacity of CM, with respect to frothing reagents (Fuerstenau and Pradip, 1982), and its variations in elemental and molecular chemistry (Holuszko and Mastalerz, 2014). The carbonate-enrobing CM influences its wettability, inhibits dissolution, and thus lowers metal recovery (Hutchins et al., 1988; Afenya, 1991, in Ofori-Sarpong et al., 2013).

Carbonaceous matter flotation applied to coals, shows that in one single deposit, the CM possesses different degrees of hydrophobicity. This leads to variable responses during flotation. Hydrophobicity strongly depends on surface properties, which vary with chemical composition, their association with host mineral (Holuszko and Mastalerz, 2014) and their morphologies and porosities (Gredelj et al.

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2009).

It is therefore important to identify the CM and to characterize its physico-biochemical characteristics, in order to develop an efficient ecological and economical metallurgical process design. Advances in analytical techniques such as QEMSCAN, can measure CM in polished sections, however, in black shales, abundant CM could be mistaken with the resin impregnation used in sample preparation. Furthermore, fine grained, intergrown CM might be difficult to detect.

The objective of this paper is to characterize carbonaceous matter that occurs as discrete occurrences (CM), but also as complex intergrowths with pyrite and manganese carbonates (CMP) using several analytical techniques including (XRD, optical microscopy, scanning electron microscopy, focused ion beam – transmission electron microscopy (FIB-TEM) analyses, QEMSCAN, electron microprobe, whole rock chemical analyses (XRF), and total organic carbon content (TOC) using Rock-Eval.

We demonstrate the limits of each method and the necessity of crossing different analytical technologies to have the most complete information at ore deposit scale. Furthermore, we propose high quality, time and cost efficient proxies, that can be used in appropriate process design.

2. Sample material

The CM-rich black shales studied here come from drill cores (COMILOG) from the Bangombé Plateau, Moanda, Gabon. These shales are of Paleoproterozoic age (2.1 Ga), belonging to the upper part of the FB series (Weber, 1968). Based on X-ray diffraction analyses, the shales are composed of dolomite and manganese carbonates with variable contents of quartz, muscovite, kaolinite, illite-smectites and pyrite (Fig. 1). Carbonaceous matter (CM) is abundant. It occurs interstitial to, and intergrown, with carbonate and Al-silicate grains (Fig. 2A, B). Under ultraviolet (UV) light, the organic resin used for impregnation that surrounds the sample particles appears green (at 20× magnification) (Fig. 2C).

3. Methodologies

3.1. Sample preparation for polished sections

Seven black shale samples were crushed to passing 1.6 mm. Specifix™ resin, mixed with hardener, was used for particle impregnation at 50 °C under vacuum. As larger particles sink to the bottom during hardening, the sections were cut vertically, positioned in the mould and again impregnated at 50 °C under vacuum to assure representative analyses. All sections were diamond polished. One polished thin section was prepared from an uncrushed rock sample.

3.2. Incident light and scanning electron microscopy

The polished sections and thin section were studied using incident light microscopy (Leica) at Université Pierre et Marie Curie, Paris, France and at the ISTO laboratory at the University of Orléans, France with a special equipment for organic matter petrography and maceral analysis. One sample was selected for further study at ERAMET Research, Trappes, France.

Carbonaceous matter-rich zones were analyzed using scanning electron microscopy in both back-scattered and secondary electron modes (ZEISS), with an EDX-Ge detector for semi-quantitative chemical analyses at 5 kV.

3.3. FIB-TEM analyses

Focused ion beam – transmission electron microscopy (FIB-TEM) analyses were performed at the GFZ Helmholtz Centre in Potsdam, Germany. The Focused ion beam (FIB) technique was used to cut slices with dimensions of $10 \times 10 \times 0.1\ \mu m^3$ for TEM. Details of the FIB milling process were given in Wirth (2004, 2009). TEM was performed using a FEI F20 X-Twin microscope with a Schottky field emitter as an electron source. The TEM mode was used to assess the bright and dark field imaging and selected area electron diffraction (SAED). A Fishione high-angle annular dark field (HAADF) detector enables Z-contrast imaging. The chemical composition of selected spots was determined with an X-ray analyzer (EDAX) with ultra-thin window and a Li-doped

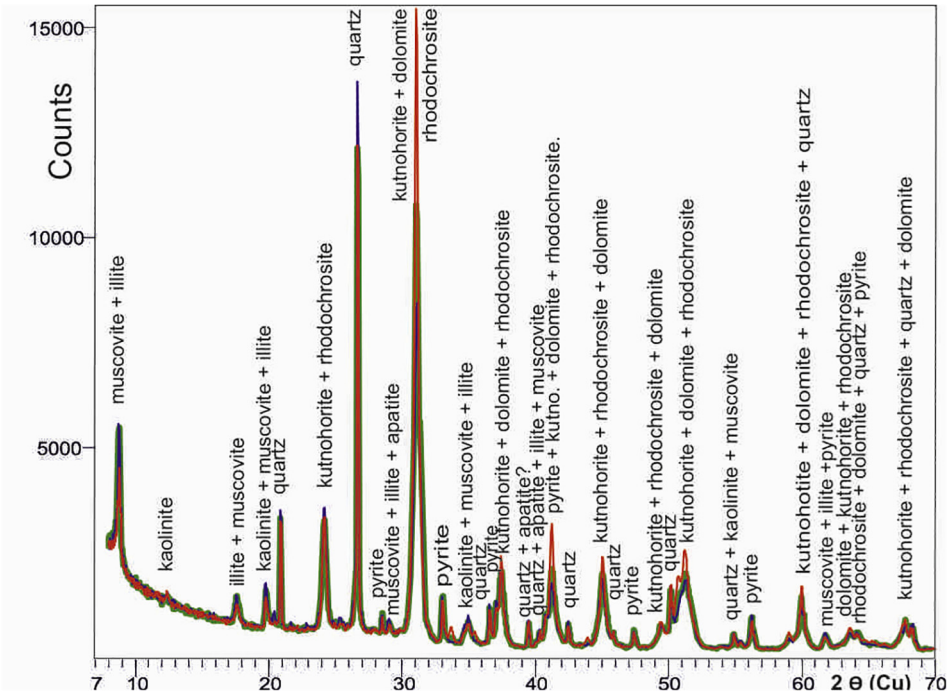

Fig. 1. X-ray diffraction pattern of the bulk mineralogy of the carbonate-bearing black shales.