

Distribution and partitioning of major and trace elements in pyrite-bearing sediments of a Mediterranean coastal lagoon

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ABSTRACT

The formation of iron sulphide minerals exerts significant control on the behaviour of trace elements in sediments. In this study, three short sediment cores, retrieved from the remote Antinioti lagoon (N. Kerkyra Island, NW Greece), are investigated concerning the solid phase composition, distribution, and partitioning of major (Al, Fe) and trace elements (Cd, Cu, Mn, Pb, and Zn). According to ²¹⁰Pb, the sediments sampled correspond to depositions of the last 120 years. The high amounts of organic carbon (4.1–27.5%) result in the formation of Fe sulphides, predominantly pyrite, already at the surface sediment layers. Pyrite morphologies include monocystals, polyframboids, and complex FeS–FeS₂ aggregates. According to synchrotron-generated micro X-ray fluorescence and X-ray absorption near-edge structure spectra, authigenically formed, Mn-containing, Fe(III) oxyhydroxides (goethite type) co-exist with pyrite in the sediments studied. Microscopic techniques evidence the formation of galena, sphalerite and CuS, whereas sequential extractions show that carbonates are important hosts for Mn, Cd, and Zn. However, significant percentages of non-lattice held elements are bound to Fe/Mn oxyhydroxides that resist reductive dissolution (on average 60% of Pb, 46% of Cd, 43% of Zn and 9% of Cu). The partitioning pattern changes drastically in the deeper part of the core that is influenced by freshwater inputs. In these sediments, the post-depositional pyritization mechanism, illustrated by overgrowths of Fe monosulphides on pre-existing pyrite grains, results in relatively high degree of pyritization that reaches 49% for Cd, 66% for Cu, 32% for Zn and 7% for Pb.

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1. Introduction

Sedimentary pyrite (FeS₂) forms via the reaction of detrital iron minerals with hydrogen sulphide, which is produced by the reduction of sulphate using organic matter as a reducing agent (Berner, 1970, 1984). The initial product of this reaction is not pyrite, but metastable monosulphides, which can be converted to pyrite via either the “H₂S mechanism” (Butler and Rickard, 2000; Rickard and Luther, 1997) or the “polysulfide mechanism” (Berner, 1970; Luther, 1991; Schoonen and Barnes, 1991; Wilkin and Barnes, 1997). Framboids are the dominant form of pyrite in recent anoxic sediments. Several theories have been proposed for their formation mechanism, ranging from biogenic to inorganic leading

to comprehensive, often debated, literature reviews (e.g. Rickard, 1970; Sawlowicz, 1993; Butler and Rickard, 2000; Sweeney and Kaplan, 1973; Wilkin and Barnes, 1997; Ohfuji and Rickard, 2005). However, the texture of framboids suggests that there is an initial stage of microcrystal nucleation and growth followed by microcrystal incorporation into framboids by aggregation (Wilkin and Barnes, 1997; Wilkin et al., 1996).

The formation of pyrite and other iron sulphide minerals, such as amorphous FeS, mackinawite, and greigite, exert significant control on the behaviour of trace elements (Morse and Luther, 1999; Burton et al., 2006). Within anoxic sediments, major and trace elements can react with sulphide and form discrete metal sulphide minerals, co-precipitate with, or absorb onto iron sulphides, and incorporate into pyrite (Morse, 1994; Morse and Luther, 1999; Scholz and Neumann, 2007; Oakley et al., 1980; Huerta-Diaz et al., 1998). Since formation of sulphide minerals requires substitution of H₂O by aqueous sulphide, the extent to which trace elements are

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incorporated into pyrite or form discrete metal sulphide minerals, depends strongly on their water exchange reaction kinetics, which in turn depends on the electron configuration of their *d*-orbital (Morse and Luther, 1999; Scholz and Neumann, 2007 and references therein). Nickel and Co, having slower kinetics of water exchange than Fe should incorporate into pyrite, whereas Pb, Cd and Zn, with faster rates of water exchange than Fe, are expected to form distinct sulphide phases, prior to the formation of pyrite (Morse and Luther, 1999). Nevertheless, elements with faster water exchange kinetics than Fe (e.g. Cd, Hg, Cu) may eventually incorporate into pyrite, as complexation with soluble ligands may differentiate metal reactivity with sulphides and thus allow their incorporation into pyrite, for example chlorocomplexes of Hg (Morse and Luther, 1999) and Cd (Davies-Colley et al., 1985); organocomplexes of Cu (Morse and Luther, 1999), or sulphide complexes of Cd (Gobeil et al., 1987), Cu, and Zn (Scholz and Neumann, 2007).

To further complicate the general patterns of trace element interactions within sulphidic sediments, apart from the structural or thermodynamic considerations reported above, the presence of other geochemical phases (clays, humic acids, authigenic carbonates) that may serve as adsorbing surfaces can significantly increase the quantities of metals that exist outside the sulphide–pyrite phases, even under conditions where metal sulphide precipitation and pyritization is expected to be favourable (Müller, 2002; Oakley et al., 1980).

The solubility of metal sulphides is low (Morse and Arakaki, 1993), and these phases are considered rather stable, as far as anoxic conditions prevail. Thus, sequestration of trace elements by authigenic iron sulphides and pyrite is considered a decisive process for the ultimate fate of these metals in the environment (Morse, 1994; Simpson et al., 2000).

The quantitative partitioning of elements among the various geochemical phases was pursued by single and sequential extraction procedures (Scoullou, 1981; Mortimer and Rae, 2000; Whiteley and Pearce, 2003; Oakley et al., 1980). The employment of sequential extraction procedures (SEP), such as the modified BCR procedure (Rauret et al., 1999), and the more targeted “pyrite-extraction” procedure of Huerta-Diaz and Morse (1990) have offered a better understanding on the exceptionally

complex, element–solid phase associations within the sediments (e.g. Müller, 2002; Huerta-Diaz and Morse, 1992; Charriau et al., 2011). More recently, powerful techniques exploiting high intensity synchrotron-generated X-rays have been adapted and allowed the direct determination of the chemical forms of major and trace elements (e.g. Hashimoto et al., 2009; Oafoku et al., 2009; Kraal et al., 2013). Although these techniques allow overcoming the problems related to the operational nature of sequential extractions, their application is restricted to heavily contaminated samples due to their relatively poor detection limits (Bacon and Davidson, 2008).

The present study aims at contributing to the understanding of trace element–solid phase associations in diagenetically active, pyrite-bearing lagoon sediments. To address the objective, we examine the distribution and geochemical partitioning of major (Al, Fe) and trace elements (Mn, Cd, Cu, Pb, Zn) in sediments of three short cores retrieved from the Antinioti lagoon (NW Greece). The study includes various chemical extractions combined with solid-state element distribution and speciation measurements by synchrotron radiation (SR) micro X-ray fluorescence (μ -XRF) and micro X-ray absorption near edge structure (μ -XANES) techniques.

2. The study area

The Antinioti lagoon (Fig. 1) is located on the island of Kerkyra (Corfu) and forms part of the homonymous wetland consisting of the shallow lagoon itself (40 ha) and marshes and wet meadows (60 ha) that extend to the southeastern part of the lagoon. Its length is approximately 1600 m on the east–west axis and less than 400 m on the north–south axis. The lagoon communicates with the Ionian Sea through two channels, one at the east of approximately 100 m length and one at the west of 200 m length, among which stands the Agia Aikaterini islet.

The hydrological regime is characterised by the micro-tidal seawater inflows and freshwater inputs that include relatively high for the Mediterranean direct precipitation (mean annual 1200 mm), runoff and drainage of the basin, including the orographic system of Pantokrator (849 m altitude), few ephemeral streams and the inputs of freshwater springs seeping at the bottom of the lagoon.

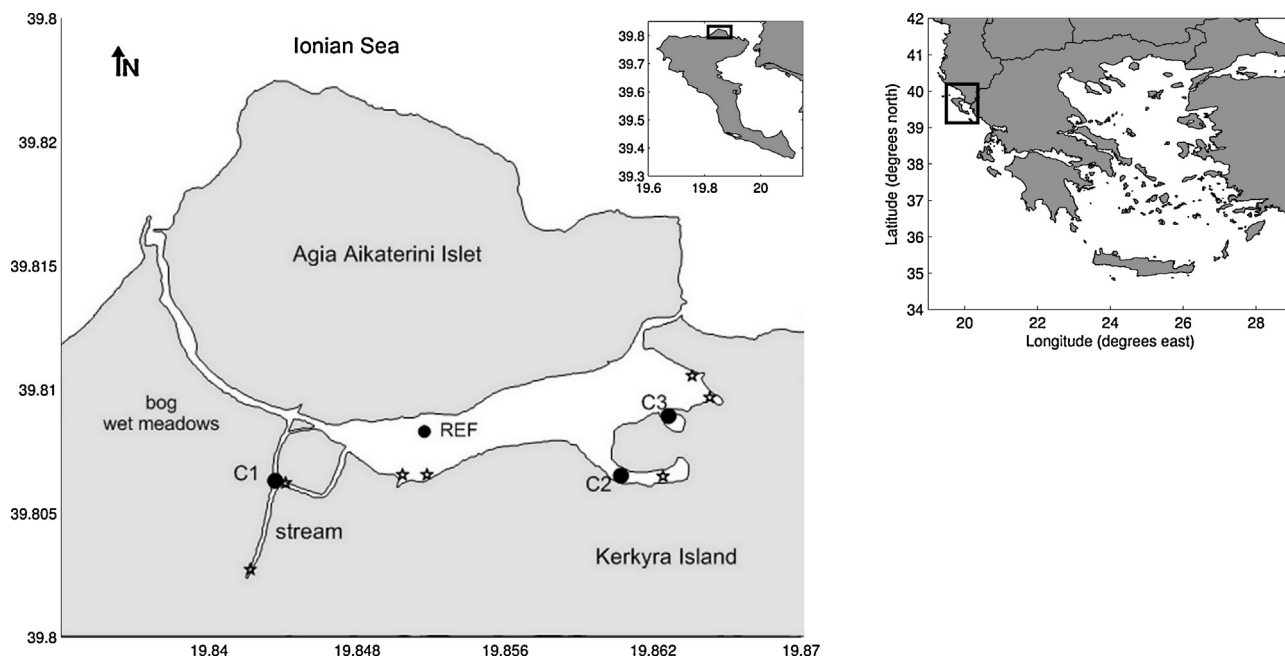


Fig. 1. Location of the Antinioti lagoon and sampling sites marked with circles. Asterisks mark the position of the subsurface groundwater seepage and the surface discharges (stream).

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