



# Poorly-crystalline components in aggregates from soils under different land use and parent material



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## ARTICLE INFO

### Article history:

Received 3 November 2015  
Received in revised form 1 April 2016  
Accepted 11 May 2016  
Available online 22 May 2016

### Keywords:

Iron  
Aluminium  
Land use  
Soil aggregates  
Amphibolite  
Granite

## ABSTRACT

Fe and Al compounds of low degree of crystallinity are important components for the development and conservation of soil structure in many soils. In this work, the influence of parent material and land use on the abundance of poorly-crystalline forms of Fe and Al was studied in six macroaggregate fractions from 28 soils. The soils selected are developed on two geological materials with very different composition: granites or amphibolites, and under two land uses: shrubland or agricultural. Poorly crystalline Fe and Al were extracted with oxalic acid–ammonium oxalate (inorganic and organic forms), and with pyrophosphate (organic forms). Soils developed on amphibolite were richer in organic matter and poorly-crystalline Fe and Al compounds than soils developed on granite. Agricultural soils were impoverished in organic carbon and organic-complexed Al with respect to shrubland soils, and enriched in inorganic poorly crystalline forms of Fe. The differences related to land use were more evident in the amphibolite soils. Aggregate stability, assessed by water-dispersible clay quantification, decreased in agricultural soils with respect to shrubland soils, in particular for those developed on amphibolite. This reduction of aggregate stability in agricultural soils is likely due to a combination of several processes: loss of organic matter, higher pH, and an overall loss of poorly-crystalline Fe and Al compounds, in particular Al-organic matter complexes.

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## 1. Introduction

Soil components controlling aggregate formation and stability are fundamental for soil properties such as infiltration capacity and permeability, water holding capacity, tilth, gas exchange, organic matter decomposition, or erodibility (Duiker et al., 2003). For flocculated soil particles to form stable aggregates, it is necessary that these particles are cemented by substances such as organic matter (OM), Fe and Al (hydr)oxides, colloidal silica or calcium carbonate. In general, OM is regarded as the key actor for soil aggregation (Tisdall and Oades, 1982) and consequently extensive research has been devoted to the relationship of OM nature and abundance to soil structure (Carter and Stewart, 1996). However, the relative importance of these cementing substances can be conditioned by the type of soil, vegetation, land use or climatic conditions (Barral et al., 1998). Recently, a number of studies are focusing on the role of other aggregation agents in situations where OM is not the main factor for aggregation, for example, in soils with very low OM contents and/or high concentrations of Fe and Al oxides or carbonates (Barthès et al., 2008; Fernández-Ugalde et al., 2013, 2014; Virto et al., 2013).

Iron and Al (hydr)oxides influence soil structure in most soils and can be particularly relevant in some cases, for example in highly-weathered tropical soils (Barthès et al., 2008). Despite their small contribution to the soil mass, Fe-(hydr)oxides are very active in aggregation due to their large surface-to-mass ratio (Eusterhues et al., 2005; Mikutta et al., 2006; Hiemstra et al., 2010; Pronk et al., 2011; Regelink et al., 2015). As a result, they have the ability to form strong bindings with clay, silt and sand particles (Arias et al., 1996; Barral et al., 1998; Sei et al., 2002) and dominate the surface area available for sorption of soil organic carbon (OC), playing an important role in its stabilization and in the formation of organo-mineral assemblages (Kaiser et al., 2011; Regelink et al., 2015). Al oxides also play a significant role in aggregation in some soils (Penn et al., 2001; Mbagwu and Schwertmann, 2006; Barthès et al., 2008; Igwe et al., 2009; Asano and Wagai, 2014), but this has been less strongly supported by the literature than in the case of Fe compounds.

Although it is well established that Fe and Al (hydr)oxides stimulate aggregation, their role is not yet completely understood. This may be due to differences in the degree of crystallinity of these compounds. Poorly crystalline Fe-(hydr)oxides have a much larger and more reactive surface area than crystalline Fe (hydr)oxides (Duiker et al., 2003; Kaiser et al., 2007). In this sense, several authors have found that crystalline Fe-(hydr)oxides are of less importance than poorly-crystalline Fe-(hydr)oxides for aggregate stabilization (Barral et al., 1992;

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Pinheiro-Dick and Schwertmann, 1996; Duiker et al., 2003; Regelink et al., 2015). Barral et al. (1992) used regression analysis and simulated rainfall to examine the stability of Galician surface soils developed over iron-rich parent materials, and found that a larger proportion of the variance in stability was explained by Fe soluble in oxalic acid  $\pm$  ammonium oxalate (poorly-crystalline forms) than by Fe soluble in dithionite-citrate (crystalline plus poorly-crystalline forms). According to Rhoton et al. (1998), Fe (hydr)oxide crystallinity explained differences in erodibility of loess-derived soils in Mississippi. Similarly, poorly-crystalline Al-(hydr)oxides or allophane contribute substantially to aggregate formation and stability in some soil types, in particular in Andosols, depending on the amounts of the respective minerals present in the soil (Asano and Wagai, 2014; Penn et al., 2001).

Poorly-crystalline Fe and Al compounds are important aggregating agents in humid climates where weathering is intense due to high precipitation, in particular in soils developed over geological materials rich in weatherable minerals such as pyroclastic or volcanic material and mafic rocks (IUSS Working Group WRB, 2014). Notwithstanding, these compounds can also be important in soils developed on other parent materials, in cool-temperate and humid climates. Soils developed on easily weatherable materials (mafic and ultramafic rocks, e.g. gabbros, amphibolites, granulites, some biotitic schists and mafic gneisses) under humid temperate conditions often display andic soil properties during the early stages of weathering, associated with the presence of large contents of Al-humus complexes and other Al-reactive forms (García-Rodeja et al., 1987; Iamario and Terribile, 2008). Later, amorphous Fe and Al compounds tend to evolve quickly from amorphous to crystalline forms in well-aerated media, unless stabilized by interaction with other soil components such as organic matter or phosphates (Duchaufour, 2001). This evolution can be affected by land use changes: several authors have observed that conversion of forest or shrubland to agricultural use leads to a loss of poorly-crystalline Fe and Al compounds (Parfitt et al., 1997; Verde et al., 2005, 2008) and consequently to an increase of their degree of crystallinity (Li and Richter, 2012).

The literature shows that poorly-crystalline forms of Fe and Al are important components for aggregation in some soils, and that factors such as soil parent material and land use can influence their role, but also that more studies strictly focused on these forms are necessary. In particular, works where organic and inorganic poorly-crystalline components are specifically studied are very unusual, to the best of our knowledge. With the objective of understanding the influence of parent material and land use on the abundance of poorly-crystalline forms of Fe

and Al we have studied the composition and stability of macroaggregates in 28 soils from a humid region in NW Spain. The soils selected for the study are developed on two geological materials with contrasted composition: granite or amphibolite, under two different land uses: shrubland or agricultural. The soils fulfil to different extents the conditions needed for the predominance of poorly-crystalline Fe and Al compounds: they are exposed to climatic conditions that guarantee a fast weathering rate, but only amphibolite soils have a favourable parent material factor (alkaline, highly weatherable rock). Therefore, the abundance of poorly-crystalline components and their relation with aggregation should be different for the soils developed over the two contrasting parent materials, as well as in soils under different land use.

## 2. Material and methods

### 2.1. Soils

We studied 28 soils from a humid region in NW Spain, developed on two parent materials: 14 on two-mica granites (soils 1–14) and 14 on amphibolites (soils 15–28). Mean annual air temperature in the area is 13 °C, and total mean annual precipitation is 1787 mm year<sup>-1</sup>, with relatively low potential evapotranspiration (50–100 mm in winter and >300 mm in summer), which results in a positive water balance (600–800 mm) (Martínez Cortizas and Pérez Alberti, 1999). For each parent material, seven soils (1–7 and 15–21) are under agricultural use, and the other seven are shrubland soils (8–14 and 22–28). At present, arable rotations alternate between forage (ryegrass and white clover) and agricultural (maize and wheat) crops, the most common rotation being a forage crop in winter and maize in summer (Verde et al., 2005). Shrublands in the area are heathlands dominated by *Ulex europaeus* L.

Amphibolite soils are located on an homogeneous amphibolitic massif in the proximity of Santiago de Compostela, at the NW extreme of the Iberian Peninsula (Fig. 1). These amphibolites are a part of the massif of mafic and ultramafic rocks known as the Ordes Complex, that also includes biotite schists, serpentinites and gabbros (Martínez Catalán et al., 1984). The amphibolites are dark, fine-grained rocks with a nematoblastic texture, composed of amphibole and plagioclase (Martínez Catalán et al., 1984). Their weathering under the climatic conditions of the region produces the quick removal of amphiboles and plagioclases, giving as a result clay-rich saprolites, dominated by kaolinite, with a residual enrichment in Fe and Al and almost complete

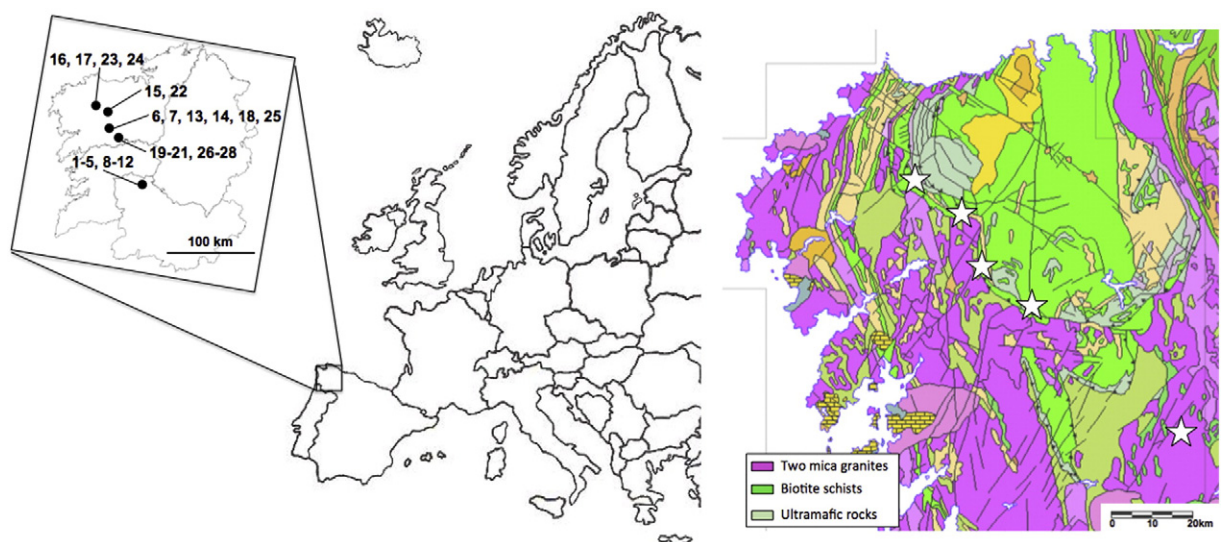


Fig. 1. Approximate situation of the soils studied and extract of the geological map of the region (IGME, 2015). Soils 1–14 are developed on granite (1–7: agricultural soils; 8–14: shrubland soils); soils 15 to 28 are developed on amphibolites (15–21: agricultural soils; 22–28: shrubland soils).

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