



# The geochemistry of calcareous forest soils in Sulaimani Governorate, Kurdistan Region, Iraq



Andrew W. Rate<sup>a,\*</sup>, Shuela M. Sheikh-Abdullah<sup>b</sup>

<sup>a</sup> School of Geography and Environmental Science, University of Western Australia, 35 Stirling Highway, Crawley 6009, Western Australia, Australia

<sup>b</sup> School of Soil and Water Sciences, Faculty of Agricultural Sciences, University of Sulaimani, Bakrajo, Kurdistan of Iraq

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## ABSTRACT

The properties of and processes in calcareous soils are important in the context of dryland soil management and moderation of atmospheric CO<sub>2</sub> by carbonate weathering. This study was conducted to determine the major and trace elemental composition in soils of the Kurdistan region of Iraq, and their geochemical features. Soil samples were taken from seven pedons, five of them from forest soils and two others from non-cultivated soils. Selected physical properties, total concentrations of elements and mineralogical properties were determined on samples from each horizon. Weathering processes in the soils are characterised by loss of Ca, Sr and several trace elements, and accumulation of less mobile elements such as Zr, Ti, and Al. The progress of carbonate weathering was best expressed using Ba/Sr and Rb/Sr ratios. Principal components analysis confirmed that distinctive geochemical differences for two profiles (significantly higher Mg, Co, Cr, Mn, and Ni) were likely to represent control by parent material, a conclusion reinforced by both mineralogical differences and the location of profiles relative to surficial geology. The other main geochemical processes differentiating the pedons were chemical weathering of carbonates and accumulation of residual elements. Calculation of absolute mass flux ( $\tau$ ) values showed that, for some profiles, concentration of mobile elements such as Na and K by evapotranspiration was potentially important, despite evidence for clay eluviation in most profiles. Absolute loss of several elements was also correlated with increased weathering as measured by Ba/Sr ratios. None of the forest soils showed enrichment-depletion ( $\tau$ ) profiles for Fe or Al consistent with podzolisation. This study highlights useful geochemical approaches to understanding chemical weathering and pedogenesis in calcareous soil profiles.

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## 1. Introduction

Soils which contain pedogenic carbonate, or which retain carbonate minerals from their protolith after substantial pedogenesis, occupy significant land areas in sub-humid to arid environments worldwide in which such soils are used for food production (IUSS Working Group WRB, 2014). The weakly acidic solution produced by dissolution of atmospheric CO<sub>2</sub> in meteoric and pore waters weathers both carbonate and silicate rocks, with a significant proportion of atmospheric CO<sub>2</sub> consumed by carbonate mineral dissolution in some soils (Clow and Mast, 2010). Mineral weathering in all soils moderates atmospheric composition over long (<10<sup>6</sup> y) timescales by consuming carbon dioxide (Chadwick et al., 1994). Weathering of carbonate rocks has been proposed as the basis of a carbon sequestration strategy (Rau et al., 2007), but the significance of carbonate mineral weathering in natural soil environments is not yet well understood. Geochemical indices of weathering can assist with understanding of carbonate weathering

processes in soils; in this context, calcareous loess environments have been evaluated recently (Buggle et al., 2011; Finke and Hutson, 2008), but no similar evaluation exists for soils developed from carbonate residuum. Given the importance of calcareous soils in semiarid agriculture and their potential for carbon sequestration, numerous studies address their pedogenesis (Gile et al., 1966; Buggle et al., 2011; Finke and Hutson, 2008; Khormali et al., 2003; Owliaie et al., 2006). Surprisingly few studies on the pedogenesis of calcareous soils have employed either multielement geochemistry or calculation of elemental mass balance; those that have (Chen et al., 2011; Ebeling et al., 2016) address environments or contexts (paddy soils, palaeosols) not directly relevant to this work.

Aeolian processes may also be important in adding new material to soil profiles in (semi)arid regions (Amundson, 2005); however, the importance of aeolian inputs in the soils of the Sulaimani region of NE Iraq has not been determined. Buringh (1960) summarised the early state of knowledge by concluding that loess-like deposits in northwestern Iraq contained material of fluvial, colluvial, and aeolian origin. Kurter (1991) recognised that glaciers do not exist in Iraqi mountains, so that a source of true loess does not exist. Although Hojati et al. (2012) showed that atmospheric dust generation from Iraqi deserts may be

\* Corresponding author.

E-mail addresses: [andrew.rate@uwa.edu.au](mailto:andrew.rate@uwa.edu.au) (A.W. Rate), [shuelamohamade@yahoo.com](mailto:shuelamohamade@yahoo.com) (S.M. Sheikh-Abdullah).

substantial, earlier work by Tsoar and Pye (1987) concluded that desert dust accumulation rates are too slow for loess deposits to form. Aeolian deposits were considered “poorly developed” in Iraq and Kuwait, and the predominant north-westerly summer wind direction would limit aeolian transport of material to Iraq’s north-eastern region (Tsoar and Pye, 1987). The evident uncertainty about the role of aeolian processes in the Sulaimani region of NE Iraq suggests that new data are needed. Geochemical and mineralogical data can provide some indications of aeolian inputs, but this is largely beyond the scope of this work.

It is well established that soil-forming processes result in losses, gains or redistribution of elements, and that not all elements are affected in the same way (Amundson, 2005). Concentrations of elements in soils reflect, first, the composition of parent material and, second, the effects of weathering including biological processes (Brantley et al., 2007). In the early stages of soil formation, the elemental composition of soil is most likely to be related to the composition of its parent material. For more mature soils, however, the chemical and mineralogical composition strongly reflects the effects of chemical weathering and pedogenic losses, gains, transformations and translocations (Brimhall and Dietrich, 1987; Brantley et al., 2007). Soil chemistry and mineralogy is therefore more likely to reflect the dominant soil forming factors, especially climate and the vegetation present in the climate-biome complex (Schaetzl and Anderson, 2005). Nevertheless, even very old or intensely altered (e.g. lateritic) soil or regolith may still bear a geochemical signature of its parent material, especially for elements originally present in refractory minerals or which may form very insoluble secondary phases (Anand and Butt, 2010; Du et al., 2012).

A few trace elements (e.g. Li, Sr) are present at higher concentrations in carbonate parent materials than igneous or other sedimentary rocks, but calcareous soils and parent materials tend to have lower concentrations of many trace elements (Kabata-Pendias, 2011). Some elements (e.g. Ba, Co, Mn, Rb) may be concentrated during chemical weathering and pedogenesis of calcareous parent materials, while others (e.g. Sr) become depleted (Buggle et al., 2011; Kabata-Pendias, 2011).

In ecosystems with low inputs and without any fertilization or soil amendment by humans, the nutrients available to plants come from atmospheric inputs and weathering of soil minerals. This is mainly the case with forest ecosystems, which are very efficient at recycling major nutrients (Badeau et al., 1999). Other elements, such as Si, Fe, Al, and some trace elements, are also recycled by the forest vegetation and such recycling can play a major role in soil genesis and the redistribution of elements (Brantley et al., 2007; Lucas et al., 1993; Rose et al., 1993).

It is clear that multiple processes act simultaneously to produce the distribution of elemental concentrations and mineral assemblages observed in any individual soil profile, and also that these element distributions can preserve information about the pedogenic history of the soil. The multivariate signal yielded by elemental composition of soils can be useful for interpreting and categorizing their properties and processes involved in their formation (e.g., Muller et al., 2008). The objectives of this research were therefore: (i) to determine the elemental and mineralogical composition of some calcareous soils in Iraqi Kurdistan, and analyse their interrelationships; (ii) to determine the redistribution of some elements related to pedogenesis; (iii) to evaluate geochemical indices of weathering appropriate to the calcareous soils, and (iv) to evaluate the use of geochemical data to resolve uncertainties about the genesis of the soils studied: specifically, the identity of soil parent material(s), and the contributions of aeolian processes.

## 2. Materials and methods

### 2.1. Description of field sampling locations

Soil was collected from the Sulaimani region of Northern Iraq (Fig. 1). This region is characterised by a semiarid Köppen-Geiger CSa dry-summer subtropical climate with winter-dominant rainfall (mean maximum

temperatures January 3.8 °C, July 31.3 °C). Maximum mean monthly wind speed is 33 km/h in July. Topography is hilly with variable slope (altitude > 800 m; Fig. 1 and Table 1), with soils generally classified as Kastanozems or Xerolls (IUSS Working Group WRB, 2014), having reduced thickness on steeper slopes. Plantation forest vegetation was present on most sites, which are therefore considered to be ‘cultivated’ in this study, with uncultivated grassland on the two comparison sites at Dukan (Profile 3) and Goizha (Profile 7) (Table 1). The parent materials of most profiles sampled were derived from limestones of varying textures and mineralogy (Kometan, Gulneri, Doka, and Balambo formations), with variable outcrop of alternating calcareous shales and sandstones (Kolosh and Tanjero formations, which contain material derived from mafic and ultramafic igneous rocks) (Hassan et al., 2015; Sissakian and Fouad, 2015). Much of the parent material has been reworked by geomorphological processes; for example, the land surface around Sulaimani City, which includes the Bakhtyary and Goizha profiles, is largely composed of alluvial fans (Karim, 2011).

### 2.2. Sample collection

Soil samples were taken from 7 pedons (1 and 5), 2, 4, 6, (3 and 7) from pine forest, oak forest, cypress forest, olive forest and uncultivated soils respectively. Following identification of soil horizons, a total of 43 soil samples were collected from each horizon in the profiles according to Petersen and Calvin (1986). Composite horizon samples were air dried, then sieved through a 2 mm mesh.

### 2.3. Laboratory analyses

#### 2.3.1. Physico-chemical analyses

Some physico-chemical properties of whole soils were determined. The particle size distribution was determined using the pipette method described by Van Reeuwijk (1992). Soil pH was determined using the saturated paste method (Page et al., 1982), and EC was determined according to van Reeuwijk (1992). Total CaCO<sub>3</sub> equivalent was determined according to the method described by Rowell (1994), while ‘active’ CaCO<sub>3</sub> was determined by reaction with 0.2 M ammonium oxalate solution to precipitate calcium oxalate, with the unreacted ammonium oxalate determined by titration with potassium permanganate according to Kozhikov and Yakovleva (1977). Soil organic matter was determined using the Walkley-Black wet digestion method (van Langen, 1993). Cation exchange capacity (CEC) was determined using the fixed-pH ammonium acetate method of Ryan et al. (2001).

#### 2.3.2. Total elemental analysis

Soil samples were finely ground and dried at 105 °C for 2 h, then 0.1000 g of sample was fused with 0.7000 g of lithium metaborate/tetraborate flux at 1050 °C for 30 min in a platinum crucible. Fusion beads were dissolved in 1 mol/L HCl, and Si, Fe, Ca, Mg, Mn, Na, Cr, Cu, Ni, Co, Sr, As, Al, Ti, Zr, Zn, K, V, Ga, Ba, Be, Rb, Nd, Ce and Pb were determined on the resulting solutions by ICP-OES (Perkin-Elmer Optima 7300 DV). Data were assessed for accuracy and precision using reagent blanks and a certified reference material (OREAS-43P; Ore Research and Exploration, 1997).

#### 2.3.3. X-ray diffraction (XRD)

Samples of the soil clay fractions were obtained by sedimentation following dispersion of the ≤2 mm fraction of soil in 0.25% Calgon (alkaline sodium hexametaphosphate) solution. The resulting clay suspensions were used to prepare basally oriented samples by suction through porous ceramic plates prior to XRD pattern acquisition from 2° to 30° 2θ. A portion of the clay suspension was also dried prior to random powder XRD pattern acquisition from 3° to 70° 2θ. All XRD patterns were collected using CuKα radiation on a Philips PW 1830

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