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Barium content of paleosols from Central Italy

Contenido en bario de algunos paleosuelos de Italia Central
Conteúdo em bário de alguns paleossolos da Itália Central

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ABSTRACT

A paper published in 2013 concerning the elemental composition of 50 paleosols from Central Italy (Tuscany and Abruzzo) noted that Barium values were exceptionally high, a fact which could be not justified by the presence of neighbouring outcrops of igneous rocks. This current paper aims to explain the origin and significance of barium enrichment in these Pleistocene paleosols (Xerults, Xeralfs, Udalfs and Xerepts) formed on alluvial siliciclastic deposits mainly derived from sandstones and shales and, in a few cases, insoluble residues of Mesozoic carbonate rocks. Ba content was considered in relation to the molecular weathering ratio, soil pH and total Mg content. A qualitative inverse correlation was suggested between Mg and Ba for most soils. Maximum Ba values were found both in acid and alkaline soils, while minimum values were observed in neutral soils. This suggests the existence of different pedoclimatic environments. The acid soil solution supports the Ba release from minerals and soil components and its precipitation in the presence of SO_4^{2-}, clays and Fe/Mn nodules, whereas other bases are removed. In contrast, the soils during seasonal low humidity periods or extended events of drought have a different pH: the soil solution then has a higher base concentration and therefore a greater likelihood of Ba precipitation bound to clays, metal oxides or even as insoluble sulphate (barite). Thus the soils with higher and lower pH are enriched in Ba both directly and indirectly in relation to ionic strength of the soil solution. The significant enrichment in Ba is ascribed to intense and very long pedogenetic processes during past climatic conditions of a wet- warm subtropical type, which acted on the Italian paleosols of Pleistocene age. The recurring shrink-swell pattern would have increased the rate of chemical weathering, the rate of barium release in the soil solution and its subsequent immobilisation in neoformed complexes as barite and others.

RESUMEN

En 2013 se publicó una investigación sobre la composición elemental de la fracción < 2 mm de 50 paleosuelos en Italia central (Toscana y Abruzzo). La investigación señaló, sin llegar a explicarlo, valores excepcionalmente altos de bario en todos los suelos, que no se justificaban por la presencia de afloramientos cercanos de rocas ígneas. La presente investigación tiene como objetivo explicar el origen y significado del enriquecimiento de bario en estos paleosuelos (Xerults, Xeralfs, Udalfs y Xerepts) formados en depósitos aluviales silico-clásticos pleistocenos, derivados principalmente de areniscas y esquistos del Terciario y, en algunos casos, de residuos insolubles de rocas carbonatadas del Mesozoico. Se ha relacionado el contenido de bario con el índice de alteración molecular (WMR), con el pH del suelo y, por último, con el contenido total de Mg. Los resultados revelan que los valores máximos de Ba se encuentran en los suelos más ácidos y en los más básicos, mientras que los valores mínimos aparecen en

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los suelos con reacción neutra. Al mismo tiempo existe una correlación cualitativa inversa entre Mg y Ba en la mayor parte de los suelos. Se plantea la hipótesis de la existencia de diferentes ambientes edafoclimáticos. Por una parte, la solución ácida del suelo ha favorecido la liberación de bario de minerales y de componentes del suelo y su posterior precipitación en presencia de SO_4^{2-}, arcillas y nódulos de Fe/Mn, mientras que las otras bases se han eliminado. Por otra parte, bajo condiciones de baja humedad estacional o de largos periodos de sequía la reacción del suelo no es tan ácida: la solución del suelo tiene una mayor concentración de bases y por lo tanto una mayor probabilidad de inmovilización de Ba asociado a arcillas, óxidos metálicos o incluso como sulfatos (Barita). Así, los suelos con pH en los rangos más ácidos y más básicos, en comparación con los neutros, se enriquecen en Ba directa o indirectamente en relación con la fuerza iónica de la solución del suelo. El significativo enriquecimiento en Ba se atribuye a procesos edafogenéticos muy largos e intensos durante condiciones paleoclimáticas de tipo subtropical húmedo-cálido durante los cuales se formaron los paleosuelos italianos del Pleistoceno. La continua alternancia de movimientos de distensión y contracción de las arcillas del suelo seguramente aumentaron la velocidad de la alteración química, la posterior liberación de bario en la solución del suelo y, finalmente, su consecuente inmovilización en forma de compuestos neoformados como Barita y otros.

RESUMO

Em 2013 foi publicado um artigo com uma investigação sobre a composição elementar da fração < 2 mm de 50 paleossolos na Itália central (Toscana e Abruzzo). Essa investigação observou, sem contudo dar explicação para o facto, valores excecionalmente elevados de bário em todos os solos, valores esses não justificáveis pela presença próxima de afloramentos de rochas ígneas. Este estudo tem como objetivo explicar a origem e o significado do enriquecimiento em bário destes paleossolos (Xerults, Xeralfs, Udalfs e Xerepts) formados em depósitos aluviais silicoclásticos pleistocénicos, derivados principalmente de arenitos e xistos do Terciário e, nalguns casos, de resíduos insolúveis de rochas carbonatadas do Mesozóico.O conteúdo em bário parece estar relacionado com o índice de alteração molecular (WMR), com o pH do solo e, por último, com o teor total de Mg. Os resultados revelam que os valores máximos de Ba surgem nos solos mais ácidos e nos mais básicos, enquanto que os valores mínimos surgem nos solos de reação neutra. Para além disso, é sugerida uma correlação qualitativa inversa entre os valores de Mg e Ba na maioria dos solos. Neste sentido, é levantada a hipótese da existência de diferentes ambientes pedoclimáticos.A solução ácida do solo favorece a libertação de bário de minerais e de componentes do solo e sua posterior precipitação na presença de SO_4^{2-}, argilas e nódulos de Fe/Mn, enquanto que as outras bases são eliminadas. Foram alcançadas condições com diferentes valores de pH quando os solos foram submetidos a períodos de baixa humidade ou períodos de grande seca; a solução do solo apresentava então uma concentração mais forte em bases e, como tal, uma maior probabilidade de precipitação de Ba associada a argilas, óxidos metálicos, ou mesmo como um sulfato insolúvel (Barita). Assim, os solos com valores de pH nas gamas mais ácidas e mais básicas, em comparação com os neutros, sofrem um enriquecimento em Ba direta e indiretamente relativamente à força iónica da solução do solo. Este significativo enriquecimento em Ba é atribuído a processos pedogenéticos de grande duração e intensos durante antigas condições climáticas de tipo subtropical húmido que atuaram durante o desenvolvimento dos paleossolos italianos do Pleistocénico. A contínua alternância de movimentos de distensão e contração das arglias do solo aumentaram seguramente a velocidade de alteração química, a posterior libertação de bário na solução do solo e, finalmente, a sua consequente imobilização na forma de complexos neoformados como a Barita e outros.

KEY WORDS
Barite, ionic strength of soil solution, pedoclimatic environments

PALABRAS CLAVE
Barita, fuerza iónica de la solución del suelo, ambientes edafoclimáticos

PALAVRAS-CHAVE
Barita, força iónica da solução do solo, ambientes pedoclimáticos

1. Introduction

In 2013 a paper concerning the natural uranium content of Fe/Mn nodules from 50 paleosols of Central Italy (Magaldi et al. 2013) was published (**Figure 1**). Principal component analysis (PCA) indicated that association between the trace elements was determined by the composition of different parent materials from which paleosols originated. Only uranium and in particular barium, could not be grouped with other elements. It was also noted that Ba values were exceptionally high in all soils. These values were not justified by the presence of neighbouring outcrops of igneous rocks or any contribution of past or actual winds.

Barium is an important element in the Earth's crust, with an average content of 425 mg/kg, as a component of many igneous and clastic silicate rock types (Hanor 2000). The Ba content of soils in semiarid sub-tropical regions is about 400 to 1000 mg/kg, compared to maximum values of 2000-3000 mg/kg in humid tropical regions (Aubert and Pinta 1971). In podzolic soils in Poland the content is 85 to 410 mg/kg (Jeske 2013). According to USEPA data, the mean value for world soils is 430 mg/kg. In soil solutions, Ba^{2+} ions can eventually react with sulphate ions to form barite ($BaSO_4$), and with bicarbonate to form witherite ($BaCO_3$).

This paper aims to explain the Ba enrichment in the < 2 mm fraction of 50 paleosols formed on alluvial siliciclastic deposits mainly derived from Tertiary sandstones and shales and, in some cases, insoluble residues of Mesozoic carbonate rocks.

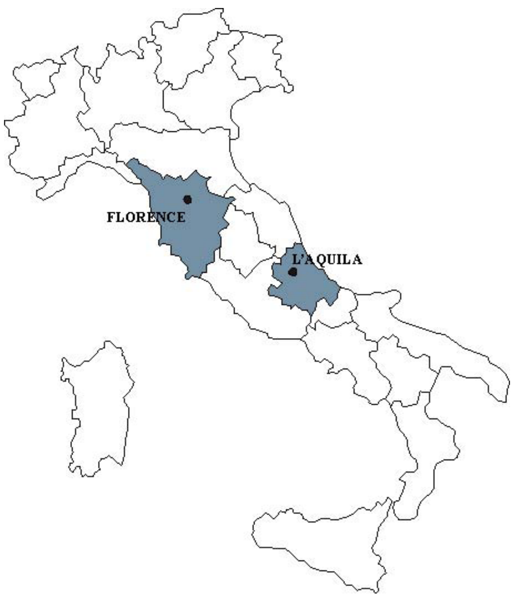

Figure 1. Italian regions where paleosols were collected. Most of pedogenetic parent material in Tuscany (Florence) is sand and gravel derived from siliciclastic Tertiary rocks and less frequently Mesozoic carbonate materials. The Mesozoic and Tertiary calcareous rock of Abruzzo (L'Aquila) are more widespread compared to Tertiary sandy and marly flysch.

2. Materials and Methods

It was assumed that all paleosols collected in Tuscany and Abruzzo (59 samples from 50 profiles) formed on terrigenous clastic sediments during the Pleistocene and Pleistocene/ Holocene (Figure 1). The paleosols on fluvial terraces (60%), alluvial plain and fans (25%), hillslopes and talus (15%) were classified (Soil Survey Staff 2014) as Xeralfs and Xerults (45 samples), Udalfs (8 samples) and Xerepts (6 samples). Data analysis for Xeralfs and Xerults, which included some Palexeralf and Palexerults, was performed together because in the sampled areas of Tuscany their differences were poorly expressed and sometimes a clear boundary was difficult to identify (cfr. Mazzanti and Sanesi 1987). Udalfs also included some Paleudalfs .

For the B horizon of each paleosol (< 2 mm), major (Al, Ca, Mg, Na, K, Fe, Mn) and trace elements (Li, Cr, Co, Ni, Cu, Zn, Ba, Pb) were determined by flame absorption spectrometry using the Varian Mod. 240 FS, Varian Mod. 240 Z and Jena Mod 300 AA devices. Complete elemental analysis was carried out on large nodules by x-ray spectroscopy. The following analyses were taken into consideration:

1. Molecular weathering ratio (Retallack 2001):MWR=Al_2O_3/(CaO+MgO+Na_2O+K_2O).

2. Soil pH (soil:H_2O = 1:1) coded as the following classes after Schoeneberger et al. (2002), with modifications: 10 = pH < 4.4; 20 = pH 4.4-5.0; 30 = pH 5.1-5.5; 40 = pH 5.6-6.0; 50 = pH 6.1-6.5; 60 = pH 6.6-7.3; 70 = pH 7.4-7.8; 80 = pH 7.9-8.4; 90 = pH 8.5-9.0.

3. Soil Ba content (mg/kg).

4. Soil Mg content (mg/kg).

3. Results

As shown in Table 1a, the molecular weathering ratio is able to characterise soils with (paleo) argillic horizons typical of soil environments very different to those of today. The Middle Pleistocene Xeralfs and Xerults of Italy (Magaldi 1979; Cremaschi 1987) are representative of a past strong Mediterranean or subtropical climate with marked seasonal differences, whereas the Late Pleistocene Udalfs testify to prolonged soil moisture during the year. More recent are the Xerepts, which were probably formed from the erosion of the above soils during the Pleistocene/Holocene period. Average Ba contents of 3 soil group are shown in Table 1a, together the Ba content of selected Fe/Mn nodules from 3 paleosols of Xeralfs + Xerults Group (Table 1b).

Ba content in relation to pH was considered for all soils (Figure 2), for Xeralfs + Xerults (Figure 3), for Udalfs (Figure 4), and for Xerepts (Figure 5).

Finally, Ba content was related to Mg content because, according to Robins et al. (2012) and Hanor (2000), Mg ions may increase barium mobility in soil (Figure 6).

Table 1. a) Molecular Weathering Ratio (MWR) and Ba average value for all soils; **b)** Ba and Sr contents of 3 large Fe/Mn nodules from selected paleosols

a) Nº Samples	MWR	Soil	Ba(mg/kg)
45	1.88	Xeralf + Xerult	3477
8	4.16	Hapludalf	5109
6	1.59	Xerept	5433
b) Fe/Mn nodule	Ba (mg/kg)	Sr (mg/kg)	Ratio Ba/Sr
Palexeralf-Palexerult	355	67	5.3
Typic Paleudalf	335	52	6.5
Typic Haploxeralf	864	64	10.6

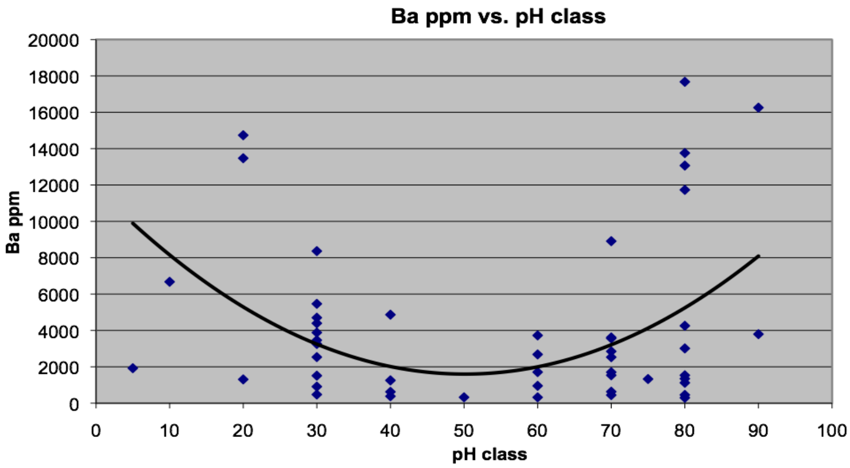

Figure 2. Ba content in relation to pH classes for all considered samples.

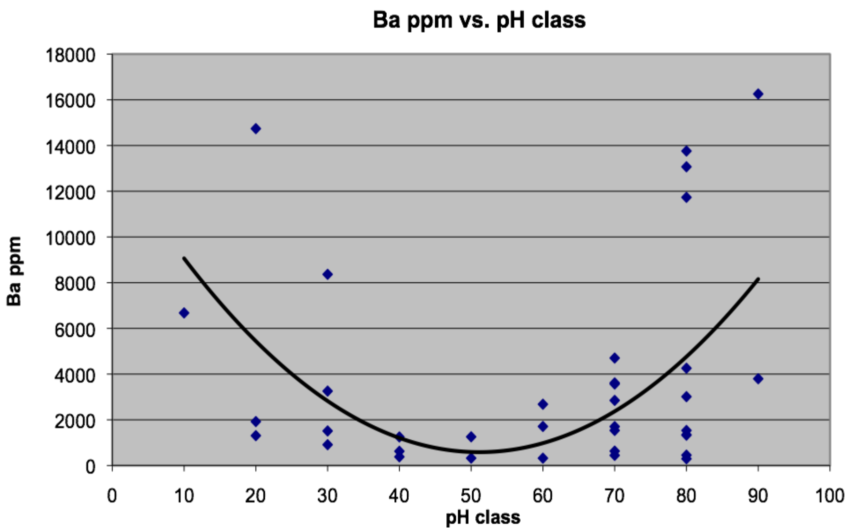

Figure 3. Ba content in relation to pH classes for Xeralf + Xerult samples.

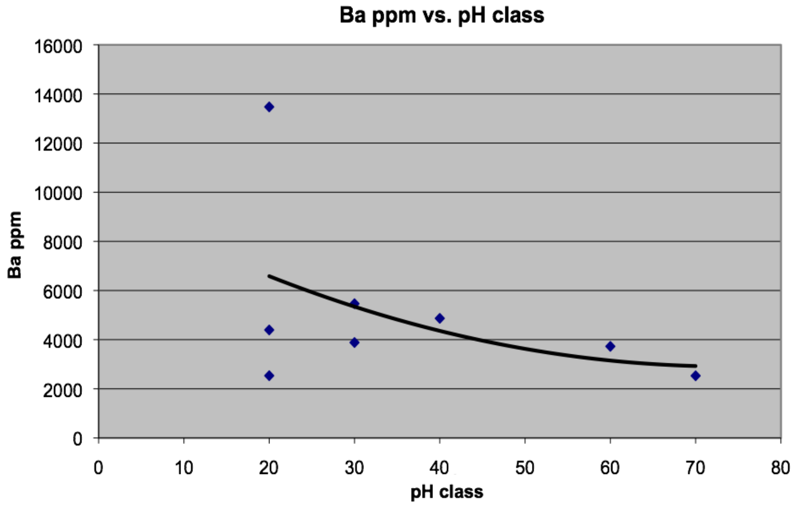

Figure 4. Ba content in relation to pH classes for Udalf samples.

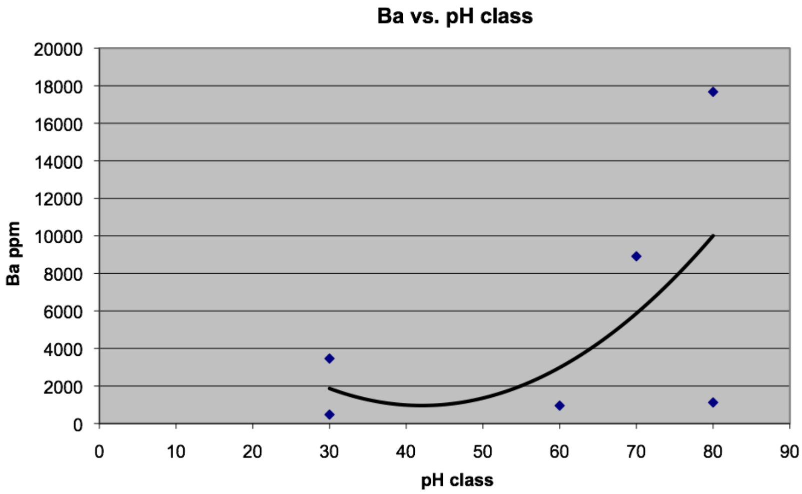

Figure 5. Ba content in relation to pH classes for Xerept samples.

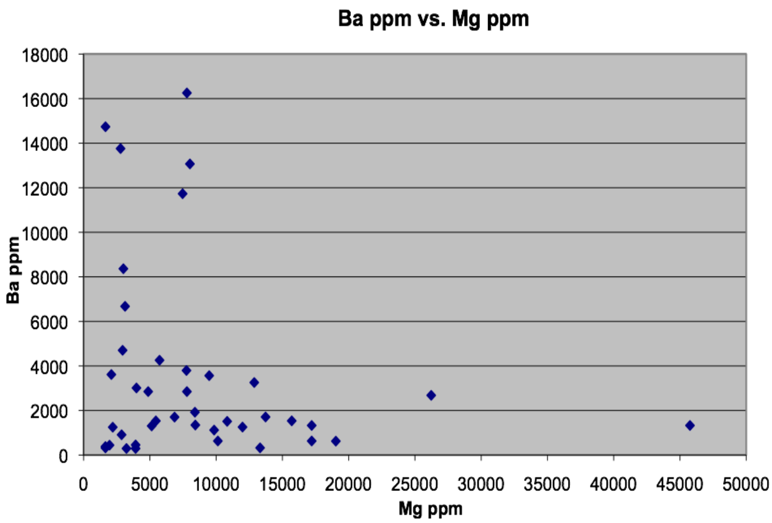

Figure 6. Ba content in relation to Mg content for all samples.

4. Discussion

Ba values are higher than those reported for sedimentary rocks and soils. For Xeralfs + Xerults the Ba values correspond to the maximum world values, while Hapludalf and Xerept are double world values. Ba/Sr ratios of some nodules indicate strong hydrolysis processes in Xeric Alfisols (Retallack 2001). A first comparison between the averages obtained for the groups of soil clearly revealed that Ba tends to be more abundant in soils less altered and more recent, in a ratio 1.7 (Udalfs) and 2.1 (Xerepts) with respect to Xeralfs + Xerults. Ba has maximum values both in the acid and alkaline classes, while the minimum was observed for neutral values (**Figure 2**). This trend is clearly shown by Xeric Alfisols and Ultisols groups (**Figure 3**) while a roughly negative correlation between pH and Ba seems to characterise the Udic group (**Figure 4**). If the trend due to automatic interpolation can be assumed as significant, then Ba indirectly increased because the acid soil conditions removed most of other cations.

On the other hand the few samples of Xerept (**Figure 5**) perhaps suggest a positive but weak correlation.

In relation to Mg content, a reverse trend is present for the whole set of samples (**Figure 6**).

The distribution of Ba in relation to pH classes qualitatively supports the existence of two different pedoclimatic environments. Both acid and basic soils have higher Ba content than soils characterized by neutral pH. The strong acid soil solution has a low ionic strength which supports the Ba release from the exchange complex but at the same time it causes the subsequent precipitation of crystalline complexes in the presence of SO_4^{2-} ions, therefore Ba can persist in the soil while other bases are removed (Kaur 2013). Then it is suggested that examined soils could contain Ba as authigenic barite crystals and/or Ba carbonate (witherite). Unfortunately this was not analysed when samples were collected some years ago. Moreover, during alternating phases of seasonal reducing conditions, Ba compounds can be dissolved and consequently Ba adsorbed by clays, Fe/Mn nodules and also plant roots (Magalhaes et al. 2012; Jeske 2013).

The effect of low pH conditions seems to be more evident in Hapludalfs as shown by **Figure 4** where Ba increases as pH decreases.

The presence of Barite in soils worldwide (mainly paleosols or strongly weathered soils) was previously referred to by Beattie and Haldane (1958) in some *parna* soils of New South Wales. A detailed list of reports on this topic has been presented by Brock-Hon et al. (2012). Authigenic barite crystals were found in a Typic Halustult from Peru by Stoops and Zavaleta (1978) and by Ferrari and Magaldi (1978) in a Pleistocene Aquic Hapludalf from areas very close to those we sampled.

Different pH conditions are reached when the soil is on seasonal low humidity periods or even some extended events of drought for its xeric environment: the soil solution then lodges a high ionic strength, stronger bases concentration and therefore a greater likelihood of Ba precipitation bound to clays, metal oxides or even as insoluble sulphate salt (Brock-Hon et al. 2012; Kaur 2013).

So the paleosols with an argillic B horizon with high and low pH values, are enriched in Ba both directly and indirectly, in relation to ionic strength of the soil solution. No particular tendency, due to the small number of samples, was noticed in the Xerepts group, except a probable enrichment similar to that of higher pH soils.

According to Deutsch (1997) the Mg occurrence in soil increases the Ba solubility and its mobility in alkaline environments. This suggests that where Mg content is high, mainly due to clays and organic matter, Ba is easily mobilised from soil, whereas the opposite happens when Mg is scarce, so Ba is able to precipitate or be fixed by clays and/or Fe/Mn nodules.

5. Conclusions

The examined soils revealed a significant enrichment in Ba not only due to the special composition of parent materials but also the intense and very long pedogenetic processes. Tertiary sandstones and shales, the main parent materials of these soils, have lower Ba contents than examined samples. So a considerable enrichment has been reached, especially in soils with a high cation exchange complex and high calcium carbonate content like most Xerepts (Kaur 2013). Wet-warm subtropical paleoclimatic conditions acted on the Italian paleosols during Pleistocene inter-glacial periods, providing favourable conditions for strong weathering because of repeated wet and dry cycles. The recurring pattern of swelling-shrinking likely increased the rate of chemical weathering and the rate of physical abrasion of mineral grains. These in turn released barium from minerals into the soil solution. Ba ions usually could associate with SO_4^{2-}, and precipitate as barite ($BaSO_4$) as was found in some paleosols.

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