Genesis of calcic concentrations in Arguidolls of the Argentinian Pampa

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Abstract
The characteristic morphology of pedogenic calcic accumulations in the Argentinian Arguidolls were studied in the southern east part of the Buenos Aires province; their distribution down the soil profile and mechanism of their formation were examined. In the monolithic samples the carbonate collomorphic (cryptocrystallic) films and carbonate tubes were examined by scanning electronic microscope observations. The origin of these carbonate accumulations is chemical. Spheroid gypsum concentrations (framboids) located on the boundary between the A humus and Bt1 illuvial horizons are most likely biogenic. Two ways of formation for those spheroid gypsum concentrations are considered: accumulation of crystal "crusts" around less soluble mineral (probably calcite) by spherical cyanobacterial colonies or the spherical form of concentrations has been inherited from framboid pyrite concentrations from sea sediment which decayed by sulfate-reducing bacteria. It is suggested that gypsum cyanobacterial concentrations have seasonal dynamics of formation in the soil profile. They are formed in the soil profile only during dry seasons whereas in humid seasons they are dissolved and disappear from the profile.

Key Words
Gypsum spherolite, framboid, cianobacteria, endolithic colonies.

Introduction
Modern Arguidolls of Argentinian Pampa are forming on paleosols and marine, eolian, fluvial and paludal sediments. The complex history of soil formation and landscape evolution has been described in papers by Zarate (2009) and Kemp (2006): 128 thousand years ago marine sediment, usually carbonate, deposited on fine paludal silts, then on some locations these marine sediment were overlaid by fine silty deposits of fluvial/paludal genesis (before 23 thousand years ago), after that the eolian loess deposits were formed approximately 10 thousand years ago. Sometimes pedo- and lithogenesis were simultaneous. So, the parent material for modern surface soils is free carbonate loess, but underlaying layers influence soil formation.
In the Argentinian Arguidolls the secondary carbonates concentrations (hypocoatings and nodules) and/or inclusions of lithogenic limestones (Borrelli *et al*. 2009) have been described. Besides, in coastal soils biogenic calcite formation through calcium oxalate has been shown. Morphology of biogenic calcite varies from needles and tubules crystals similar to fungi hyphas to traditional rounded and micrite forms (Verrecchia *et al* 1993). In these soils biogenic transformation of pyrite (FeS_2) by sulfate-reducing bacteria occurs (Osterrieth 2005). The morphology of these concentrations is special – rounded (framboid) accumulations called after 'la framboise' in French.

Objects and methods
Profile of typical Mollisol formed on loess underlying by paleopedolith (tosca) on seaside in south-east part of Buenos-Aires province, Argentina, between 37° / 38°40' S and 59° / 57°10' E. This area is subtropical preria and nowadays use as agriculture lands.
Sampling was in three horizons: border A and Bt1, Bt2 and 2Ck – sample 1, 2 и 3, accordingly.
The sample 1 - very friable, porous, dark-grey with whitish spots and fibers;
The sample 2 – light-pale, loess with vertical fractures and root/mesofaune holes;
The sample 3 –carbonate crust ("*tosca*"), grayish-white, very dense, derives on different size carbonate concentrations.
Monolith air-dried sample were studied under binocular and scanning electron microscope. We used scanning electron microscope Jeol model JSM-6380LA. Elemental analysis was conducted by X-Ray microanalysis EDS JED-2300.

Results
The sample 1, humus black horizon contains bright-white thin coating; a reaction with 10% HCl is very local, it is possible to locate it only under binocular. Already at hundred-fold magnification the white "thin

coating" is localised in spheroliths (framboids) from 10 to 100 microns in diameter formed by perfect crystals (Figure 1, a). EDS data has shown that it is gypsum crystals, characteristic external shape also testifies to it. Sometimes these framboids are connected in chains (Figure 1, b) and have small hollows on poles. In separate framboids iron is presence (according to EDS-SPECTRA). Gypsum spheroids rise slightly above general surface of the sample. Between them the thin collomorphic (cryptocrystallic) films of calcite on alumosilicate (Figure 2, a) have been observed. Such films have been repeatedly noted by us in the soils of different regions of the world characterized by a contrast water regime with strongly pronounced period(s) of humidifying and drying (Kuznetsova and Khokhlova 2009). On the sample surface the threads and congestions of cyanobacteria are noted. On individual cyanobacterium small gypsum crystals are visible (Figure 2, b).

The sample 2. It reacts with 10% HCl very poorly, locally. Thin discontinuous carbonate tubules which have been found out under binocular, are very fragile and easily disintegrated. Carbonate concentration under a scanning electronic microscope is not revealed. Basically it is slightly carbonate matrix consisting of a mixture of alumosilicate grains, "pure" and covered by thin carbonate film (Figure 3, a). Cyanobacteria are not revealed, there are separate hyphas only. The sample 3. The most carbonate sample reacts with 10% HCl violently. The matrix is a mechanical mixture of alumosilicate grains (almost without films) and porous, imperfect calcite crystals (Figure 3, b). In small holes calcite transforms to a collomorphic film which smooths out a relief, but chaotically scattered crystals and druses prevail.

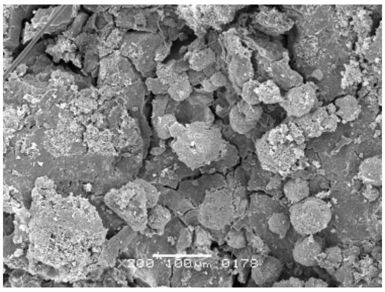

Figure 1, a

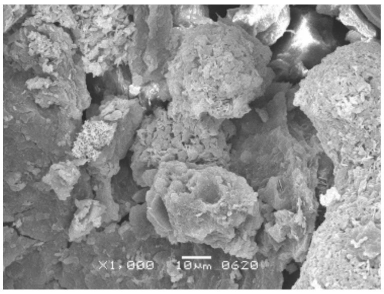

Figure 1, b

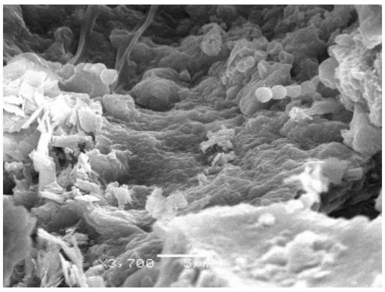

Figure 2, a

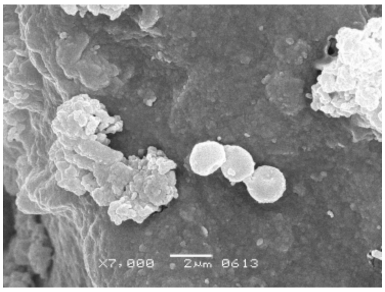

Figure 2, b

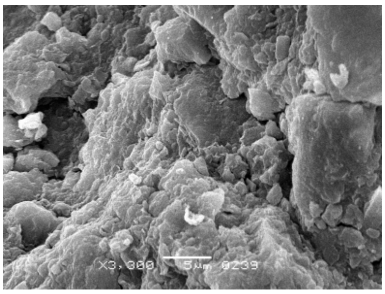

Figure 3, a

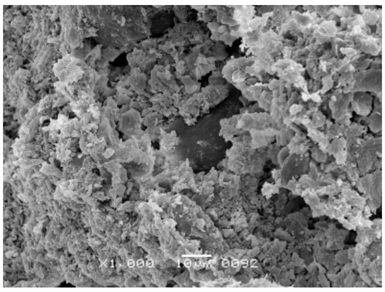

Figure 3, b

Discussion

According to obtained data on the border of humus A and Bt1 horizons the conditions for a life of cianobacteria which promote loss of a crystal deposit – biogenic soil concentrations are created. Formation of lime mats by direct participation of cyanobacteria since the Pre-Cambrian is frequently described in the scientific literature (Zavarzin 2003). Besides, spherical mats – oncoliths - are known. In them lime layers settle down not linearly, but are rounded.

In modern soils the endolithic cyanobacteria are described and found in soil gypsum crust of various deserts of the world (Dong *et al* 2007, Garcia-Pichel *et al* 2001). Similar cyanobacteria communities form laminae inside the gypsum horizon. Depth of colonies penetration depends on a gypsum structure that finally from possibility of water, oxygen and light penetration: in more porous samples cyanobacterial colonies permeate more deeply. It is thus underlined that cyanobacteria being extreme species can live in light and minimum oxygen conditions. Thus, cyanobacteria communities can support the biodiversity as endolithic species (Osterrieth 2005).

In the sample 1 we observed the formation of concentrations like oncolithes, not calcitic, but gypsum. Such structures in soil have not been described earlier, but their existence is quite possible. We will compare the following data for cyanobacteria concentrations on various substrata, both in modelling experiments, and in natural conditions which are indentified in the scientific literature:

- Sedimentation by individual cyanobacterium cells round itself by calcite crystals ($CaCO_3$), trona ($Na_3H(CO_3)(H_2O)$), halite (NaCl) (Howell *et al* 2005, Mikhodyuk *et al* 2008);
- Formation of roundish and layered calcite mats by cyanobacteria in natural conditions (Zavarzin 2003);
- Formation of stalactite-like structures from halite and gypsum and having of a layered structure:, around cyanobacteria colonies with gypsum, further a mixture of gypsum and halite and then pure halite (Braithwaite and Whitton 1987);
- High-grade functioning (with a closed cycle) cyanobacteria colonies in gypsum crust (Dong *et al* 2007, Garcia-Pichel *et al* 2001, Mikhodyuk *et al* 2008);
- Existence in Argentinian Arguidolls of biogenic concentrations/framboids as products of pyrite and calcite decomposition (Osterrieth 1992, 2005).

According to these data, gypsum concentrations on the bottom boundary of humus horizon have a biogenic origin. Two ways of their formation are possible.
1. Cyanobacteria colonies having the spherical form build up crystal crusts round themselves. Possibly, they occur at the change of a wet season to dry season when the concentration of soil solutions sharply rises. By analogy with a study by Braithwaite and Whitton (1987) we assume that less soluble mineral is situated closer to central part of these spherolites. Probably, this mineral is calcite.
2. The spherical form of concentrations has been inherited from framboid pyrite concentrations (Osterrieth 2005), because according to EDS-spectra iron is observed. In this case, pyrite transformation occurs step-by-step, through a number of other minerals. Calcium for formation of these gypsum framboids undertakes from an underlaying calcareous horizon (2Ck), or arrives with an atmospheric precipitation or plant waste. Sulphur appears as a pyrite decomposition product which has been described in these soils. Studying the mechanism of such transformations requires additional mineralogical modelling experiments.
In one case or another, gypsum cianobacterial spherolith is concentric with short-term life, their formation and functioning in soil is possible only during dry seasons. Most likely, during a season of rains similar biogenic concentrations we will not find out in the soil profile studied. Probably, both ways of biogenic genesis of soil concentrations studied take place and are realized on the bottom border humus horizon of Argentinian Arguidolls.

The sample 2: carbonates uplifting from underlaying horizon, only along thin tubes. Formation of macroconcentrations does not occur. Possibly, it is connected with sharp distinction in a structure of porous loess and well-packed underlaying "*tosca*" which is poorly dissolved, calcite uplifting occurs only along thin tubes in loess by roots. Thin discontinuous carbonate tubes are formed in such way. Collomorphic films are resulted from calcite precipitation during water regime changing from saturated colloidal solutions (Kuznetsova and Khokhlova 2009). In the studied soil this process occurs on phase interfaces at a microlevel when solutions cover particles as thin film, and from the observation of the concentrations (collomorpic films) obtained is also possible at micro - or even submicrolevels.

In sample 3 there is a fast recrystallization of limestone from strongly saturated solutions, the most part of the material does not move but is precipitated *in situ*. Therefore, there are no concentrations with perfect crystals and their formation is possible only in quiet conditions and from solutions with normal concentrations. The considerable admixture of alumosilicate grains comes, probably, as a reflexion of simultaneous sedimentation of limestone and loess.

Conclusion

In the studied Argentinian Argiudolls the calcium concentrations of different genesis are revealed: on the boundary of humus horizon and loess deposits cyanobacterial gypsum concentrations of a biogenic origin are described; chemogenic carbonate collomorphic films on a surface of alumosilicate matrix were observed in all samples, and, besides the carbonate tubes in loess and re-crystalled limestone in the 2Ck horizon have chemical genesis. Two modes of formation for those spheroid gypsum concentrations are considered: accumulation of crystal "crusts" around less soluble minerals (it is probably calcite) by spherical cyanobacterial colonies or the spherical has been inherited from framboid pyrite concentrations from sea sediment which were decayed by sulfate-reducing bacteria. It is likely that gypsum cyanobacterial concentrations have seasonal dynamics of formation and occurrence in the soil profile studied. They are formed and exist in the soil profile during dry seasons and in humid seasons they are dissolved and disappear from the profile.

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