**18 months Post-Doctoral position at CEREGE, Aix-en Provence, France**

**Organomineral interactions: nanoscale characterization for carbon sequestration in soils**

Social context

Land uses disrupt the natural functioning of soils, leading to degradation of soil resources. At the same time, forecasts estimate that agricultural production has to be increased by 1.85-fold to meet the food demand of 9 billion people by 2050. Agroecological practices thus have to fulfil two main objectives simultaneously—minimize soil degradation while improving ecosystem services. Agroecological strategies for restoring soil functioning mainly strive to enhance the soil organic matter pool by increasing organic matter input fluxes. We argue that future agroecological techniques should also be geared towards increasing the residence time of organic matter in soil. This would represent a win-win strategy since long-term C storage in soils is also an issue in term of climate change. This has been highlighted recently by the French Minister of Agriculture when proclaiming the launch of the "4 per 1000" project at COP 21.

Scientific context

A better understanding of the mechanisms that control organic matter stabilisation in soils is therefore needed. Mineral surfaces are suspected to play a major role in C storage in soils and the recently funded ANR “nanoSoilC” project, launched in January 2017, focuses specifically on the study of OM stabilization by organomineral interactions. We propose a conceptual breakthrough of organomineral interactions: our model no longer considers mineral surfaces as stable, but instead, subject to weathering. Weathering generates nanometric amorphous Al Si and Fe polymers with large specific surface areas and high reactivity towards organic compounds that they may stabilize on long-term timescales (Basile-Doelsch et al., 2015). The overall objective of the project is to explain the process of soil organic matter stabilization and destabilization by describing the mechanisms that control the organomineral interactions at the nanoscale. Organomineral complexes, considered at nanoscale, are called nCOMx.

Beyond the basic knowledge on soil functioning, two main outputs of this project are expected: (1) providing a hierarchy of processes controlling the C residence time to improve our capacity to understand and model long-term ecosystem services provided by organic matter in soils; and (2) providing the basis for understanding agroecological practices with respect to C storage and proposing innovation items.

The NanoSoilC ANR project

NanoSoilC focuses on mechanisms of nCOMx formation (during phases of soil formation and steady-state), and on mechanisms of nCOMx destabilization (loss of soil OM during the transition from forest to cultivated soil). These different mechanisms are addressed by complementary approaches. The project is organized in five Work Packages. nCOMx formation is addressed by experimental laboratory approaches (WP1) and field experiments (WP4). nCOMx destabilization is addressed by both laboratory (WP1) and field experiments (WP3), but also by an innovative modelling approach (WP2).

The consortium brings together four partners (CEREGE, ECOSYS, BEF and Recyclage et Risque) representing 5 French institutes (CNRS, Aix-Marseille Université, Collège de France, INRA and CIRAD). The panel of scientists provides expertise in various disciplines. It aims to bring together the science of nanoparticles (and their characterization tools) with soil science.

The post-doctoral scientific project

The main part of the work will aim at characterizing nCOMx using a multiscale approach. Characterization of such poorly ordered materials is challenging and will require a set of complementary techniques that must be sensitive to the organic and mineral phases, and most importantly to how they interact together. The objective is to characterize the morphology, chemistry and local structure of nCOMx and OM associations with the mineral constituents. The post-doctorant will perform the analyses and use the different methods with the objective of identifying the best combination of tools for characterizing and imaging synthetic and natural nCOMx.

Morphology and chemistry

A first step will consist in characterizing the nCOMx morphology and chemistry. Electronic microscopy (SEM and TEM) coupled with an energy-dispersive X-ray spectroscopy (EDX) detector will be used to characterize the morphology and chemical distribution of Al, Si and Fe. The total elemental composition will also be measured by ICP-AES for major elements as well as CHNS for total organic carbon. In case of very low amounts of C, the concentration will be measured by mass spectrometry (IRMS).

Atomic arrangement of the mineral phase in the short-, intermediate- and long-range order

The next step will consist of characterizing the mineral phases using a combination of nuclear magnetic resonance spectroscopy (NMR), X-ray absorption spectroscopy (XAS), total diffusion with pair distribution function analysis (PDF) and X-ray diffraction (XRD). The first three techniques will allow us to characterize the short- and intermediate-range order of the mineral part of nCOMx. Fe K-edge XAS along with 27Al and 29Si NMR (in the absence of iron or to characterize the iron-free fraction of the sample since iron is paramagnetic) were shown to be ideal in characterizing the early precipitation stage of Al, Fe and Si monomers in solution (sizes <5-6 Å) (Doelsch et al., 2002). The intermediate-range order (<30 Å) will be investigated by total diffusion using wide-angle X-ray scattering with pair distribution function analysis (Michel et al., 2007). X-ray diffraction will be used to characterize any crystalline phases that could have formed during the weathering process or to identify remaining primary minerals. Poorly crystalline phases will be characterized by HR-TEM and electron diffraction.

OM characterization

The organic fraction associated with the poorly ordered material will be characterized for nCOMx merged from soil sampling (natural nCOMx) with a series of techniques conventionally used for organic materials. 13C NMR will be used to characterize the main types of organic functions of OM. If necessary (presence of Fe-bearing phases), Fourier transform infrared spectroscopy (FTIR) will be used.

Mineral-OM interaction

The core part of the project, but also with the most challenging aim, will involve characterization of OM-mineral interactions. Such investigations require analytical tools that are element-sensitive, with a nano-resolution and, if possible, with some speciation information concerning both the mineral and organic species. In this regard, we propose to combine scanning transmission X-ray microscopy (STXM, (Lehmann et al., 2008; Solomon et al., 2012)) and cryogenic scanning transmission electron microscopy (Cryo-STEM) with energy dispersive X-ray (EDX) spectroscopy and/or electron energy loss spectroscopy (EELS,(Chia et al., 2012)). The recent development of Fresnel zone plates provides high spatial resolution (down to 15 nm) imaging of samples which are transparent for soft X-rays (STXM) (Miot et al., 2014). By varying the energy of the incident beam below and above the absorption edge of the elements of interest (e.g. C), it is possible to map and speciate the different constituents present in nCOMx. Cryo-TEM combined with EDX and EELS is also a neat alternative for mapping at a resolution of about one order of magnitude higher than for STXM (1-2 nm). Although not widely used, the combination of STXM and electron microscopy techniques has proved to be very efficient in characterizing organomineral complexes (Cosmidis et al., 2013; Cosmidis et al., 2014).

These characterizations will first be implemented on synthetic batch samples (implication of the post-doctorant) but will also serve for relevant selection of nCOMx samples obtained in the other WPs of the project (nCOMx from WP1 T1.3 incubation systems, nCOMx from WP3 T3.2 soils, nCOMx from WP4 T4.1 and T4.2 remediation experiments) when possible.

Contribution of NanoSoilC scientists to the post-doctoral project

The project research consortium is at the forefront in the development of operational short-, intermediate- and long-range order characterization methods of amorphous organomineral phases on the basis of advanced analytical tools. C. Levard, J. Rose, E. Doelsch, D. Borschneck, P. Chaurand, S. Legros are experts in using synchrotron facilities and NMR, with B. Devouard being an expert on electronic microscopy analyses (SEM/TEM, EDX, EELS) and high-resolution chemical mapping. I. Basile-Doelsch, PI of nanoSoilC project, will participate in the different analytical steps and contribute to the sample selections delivered by T1.1, WP3 and WP4.

The CEREGE lab is equipped with TFF, SEM-EDX, XRD, TOC and IRMS facilities. The CEREGE has broad experience in the use of synchrotron facilities, as well as in requesting and obtaining beam times at many synchrotrons (ESRF, Soleil, SSRL, APS, ELETTRA, SLS, NSLS). The team also has access to different types of facilities in Marseille (FTIR NMR, TEM-EDX and TEM-EELS), as well as to a Cryo-TEM at CEA Grenoble in the framework of the nanoID Equipex.

Conditions

The monthly net income is € 2,400 (PhD<2years) or € 2,900 (PhD>2years). Professional costs will be covered by the programm.

The work will be carried out mainly at CEREGE (Aix-en-Provence, France) with regular and frequent missions in France and abroad to carry out the analyses.

CEREGE is a research laboratory in the field of environmental sciences. It brings together scientists from various research institutes (CNRS, INRA AMU, IRD, Collège de France). It is located in the Provence Alpes Cote d'Azur region, 15 km from Aix en Provence, in a technological park dedicated to the environment. Access by bus from Aix-en-Provence and Marseille.

Required profile

The post-doctoral candidate must have a strong experience in the use of characterization of solid phase using spectroscopic methods. Expertise in TEM and / or X spectroscopy on synchrotron facilities would be particularly appreciated.

Contacts

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The selection process will start on March 1St 2017 and will continue until the position is filled. The funds are already available and the Post Doc will start as soon as possible, to the extent of administrative constraints.

Cited references

Basile-Doelsch, I., Derrien, D., Amundson, R., Balesdent, J., Borschneck, D., Doelsch, E. and Levard, C. (2015) Dynamics of organic compounds associated with non-cristalline minerals in andosols: a key for understanding long term SOM stabilization in any soils?, Soil Organic Matter 2015, Structure Origine Mechanisms, Göttingen, Germany.

Chia, C.H., Munroe, P., Joseph, S.D., Lin, Y., Lehmann, J., Muller, D.A., Xin, H.L. and Neves, E. (2012) Analytical electron microscopy of black carbon and microaggregated mineral matter in Amazonian dark Earth. Journal of Microscopy 245, 129-139.

Cosmidis, J., Benzerara, K., Menguy, N. and Arning, E. (2013) Microscopy evidence of bacterial microfossils in phosphorite crusts of the Peruvian shelf: Implications for phosphogenesis mechanisms. Chemical Geology 359, 10-22.

Cosmidis, J., Benzerara, K., Morin, G., Busigny, V., Lebeau, O., Jezequel, D., Noel, V., Dublet, G. and Othmane, G. (2014) Biomineralization of iron-phosphates in the water column of Lake Pavin (Massif Central, France). Geochimica Et Cosmochimica Acta 126, 78-96.

Doelsch, E., Rose, J., Masion, A., Bottero, J.Y., Nahon, D. and Bertsch, P.M. (2002) Hydrolysis of iron(II) chloride under anoxic conditions and influence of SiO4 ligands. Langmuir 18, 4292-4299.

Lehmann, J., Solomon, D., Kinyangi, J., Dathe, L., Wirick, S. and Jacobsen, C. (2008) Spatial complexity of soil organic matter forms at nanometre scales. Nature Geosci 1, 238-242.

Michel, F.M., Ehm, L., Antao, S.M., Lee, P.L., Chupas, P.J., Liu, G., Strongin, D.R., Schoonen, M.A.A., Phillips, B.L. and Parise, J.B. (2007) The Structure of Ferrihydrite, a Nanocrystalline Material. Science 316, 1726-1729.

Miot, J., Benzerara, K. and Kappler, A. (2014) Investigating Microbe-Mineral Interactions: Recent Advances in X-Ray and Electron Microscopy and Redox-Sensitive Methods. Annual Review of Earth & Planetary Sciences 42, 271-289.

Solomon, D., Lehmann, J., Harden, J., Wang, J., Kinyangi, J., Heymann, K., Karunakaran, C., Lu, Y.S., Wirick, S. and Jacobsen, C. (2012) Micro- and nano-environments of carbon sequestration: Multi-element STXM-NEXAFS spectromicroscopy assessment of microbial carbon and mineral associations. Chemical Geology 329, 53-73.