# Ferruginous paleosols around the K/T boundary in central-southern Sardinia (Italy): their potential as pedostratigraphic marker

Andrea Vacca[A], Concetta Ferrara[A], Ruggero Matteucci[B] and Marco Murru [A]

[A]Dipartimento di Scienze della Terra, Università degli Studi di Cagliari, Via Trentino 51, 09127 Cagliari, Italy, Email avacca@unica.it, sdapelo@unica.it, cferrara@unica.it, murrum@unica.it
[B]Dipartimento di Scienze della Terra, Università di Roma "La Sapienza", Piazzale Aldo Moro 5, 00185 Roma, Italy, Email ruggero.matteucci@uniroma1.it

**Abstract**
This paper focuses on the main morphological, chemical and mineralogical features of ferruginous paleosols around the K/T boundary in central-southern Sardinia (Italy), on their relationships with the coeval ones in south-western France, and on their potential role in stratigraphy. The main features of the Sardinian ferruginous paleosols indicate the presence of petroplinthic and pisoplinthic horizons. Pisoplinthic horizons are also present in the two considered French outcrops. Their genesis may be related to the warm and humid tropical climatic conditions occurring during Latest Maastrichtian-Lower Paleocene (Danian), which favored the formation of plinthic horizons, followed by the increasing dry conditions occurring during the Paleocene, which favored the irreversible drying of the plinthic horizons in petroplinthic and pisoplinthic horizons. On the basis of the consistent stratigraphic position, large extent and lateral continuity, these paleosols can be considered a good pedostratigraphic marker in the region and can be defined as a geosol, being helpful in the framework of extensive chronostratigraphic correlations and allowing further regional-scale morphostratigraphic correlations.

**Key Words**
Geosol, paleosols, Upper Cretaceous-Lower Paleocene, Sardinia, France

**Introduction**
Seven small outcrops of Upper Cretaceous-Lower Paleocene ferruginous paleoalterites were recently recognised and described in central-southern Sardinia (Italy) (Murru *et al*., 2007b). These paleoalterites were considered similar to those of the same age described in south-western France (Saurel *et al*., 1976; Gourdon-Platel, 1980). On these basis, Murru *et al*. (2007b) conclude that the pre-rotation position of the Sardinian-Corsican block along the south-eastern margin of the European paleocontinent allows to presume a similar climatic and environmental regional history. This paper focuses on the paleosols present within all the seven Sardinian outcrops, on their relationships with those in south-western France, and on their potential to represent a good pedostratigraphic marker for a larger area.

**Materials and methods**
The seven outcrops are scattered in various localities of central-southern Sardinia (Figure 1a). For each outcrop, described in detail in the field a main vertical profile was sampled, together with numerous other lateral levels. All the deposits lie on a Paleozoic substrate and are covered (except one) by Paleocene-Lowermost Eocene transitional to shallow-water marine sediments, sometimes with interposed lacustrine carbonate levels (Murru *et al*., 2007a). Their sedimentological characters are typical for an alluvial continental environment, with different depositional energy and varied paleomorphology. Within all the seven deposits ferruginous paleosols are present.

On the collected samples, physical, chemical, and mineralogical analyses were carried out. Bulk rock chemical composition was determined by X-ray fluorescence spectroscopy (XRF) using a Panalytical Magix Pro instrument. Al and Fe were chemically analyzed by means of optical ICP. The mineralogical composition was determined by X-ray diffraction (XRD) using a Panalytical X'pert Pro diffractometer, with Cu-Kα radiation generated at 40 kW and 20 mA. Microscopic and submicroscopic observations were made using a SEM FEI Quanta 200. Scanning electron microscopic analyses, coupled with energy dispersive spectroscopy (SEM-EDS), were performed on thin sections.

**Results and discussion**

The eastern outcrops are located at Monte Maraconis, at Ballao, and at Sant'Andrea Frius (Figure 1a). At Monte Maraconis the substrate is made up of Ordovician metavulcanites and the ferruginous paleosol shows a weak red (10R 4/4) cemented horizon, about 60 cm thick, with light gray (5Y 6/1) bleached tongues, covered by Lower Eocene conglomerates (Figure 1b) containing fragments of the cemented horizon, which testify its partial erosion. Quartz, hematite and clay minerals (illite 39%, mixed layers 24%, kaolinite 37%) are present in the cemented horizon. Al content is 3.5% and Fe content is 22.2%. The bleached areas contain quartz and clay minerals (illite 57 %, mixed layers 16%, kaolinite 27%). Al content is 7.6% and Fe content is 2%. At Ballao, on the same substrate, the ferruginous paleosol shows a dusky red (10R 3/4) cemented horizon, about 2 m thick, with light gray (2.5Y 7/2) bleached tongues (Figure 1c), covered by transitional and marine Lower Eocene sediments. Quartz, hematite, and kaolinite are the main components in the cemented horizon. At Sant'Andrea Frius, where the substrate is made up of Paleozoic metasandstones, the ferruginous paleosol shows a weak red (10R 5/2) cemented horizon with diffuse light olive gray (5Y 6/2) mottles (Figure 1d), covered by Uppermost Paleocene transitional to shallow-water marine sediments. Mineralogical analyses show the presence of quartz, hematite and illite, with traces of kaolinite. Al content is 6.3% and Fe content is 5.6%. The western outcrops are located at Villamassargia, Piolanas, Nuxis, and Guardia Pisano (Figure 1a). At Villamassargia, where the substrate is made up of Lower Paleozoic metasandstones, the ferruginous paleosol resembles very much those of south-eastern Sardinia (Figure 1e). The dusky red (10R 3/4) cemented horizon, about 4 m thick, is formed by quartz, hematite and kaolinite. Al content is 5.0% and Fe content is 12.7%. The bleached areas contain quartz and clay minerals (illite 2 % and kaolinite 98%). Al content is 4.1% and Fe content is 0.2%. The paleosol is covered by Paleocene palustrine carbonate sediments and continental deposits of the Cixerri Formation (Middle-Upper Eocene). At Nuxis the Cambrian basement is made up of dolomitic metalimestones mineralized with barite and highly karstified. The karstic cavities are filled by dark brown (7.5YR 3/3) ferruginous horizons, about 8 m thick, which are overlain by continental deposits of the Middle-Upper Eocene Cixerri Formation (Figure 1f). Three main horizons are recognizable in the ferruginous sequence preserved in the karstic cavities: a well lithified ferruginous dark brown horizon, a caothic well lithified ferruginous dark brown horizon, and a pisolithic horizon. The mineralogical analysis shows the presence of abundant hematite, kaolinite, and barite, with some goethite and quartz.

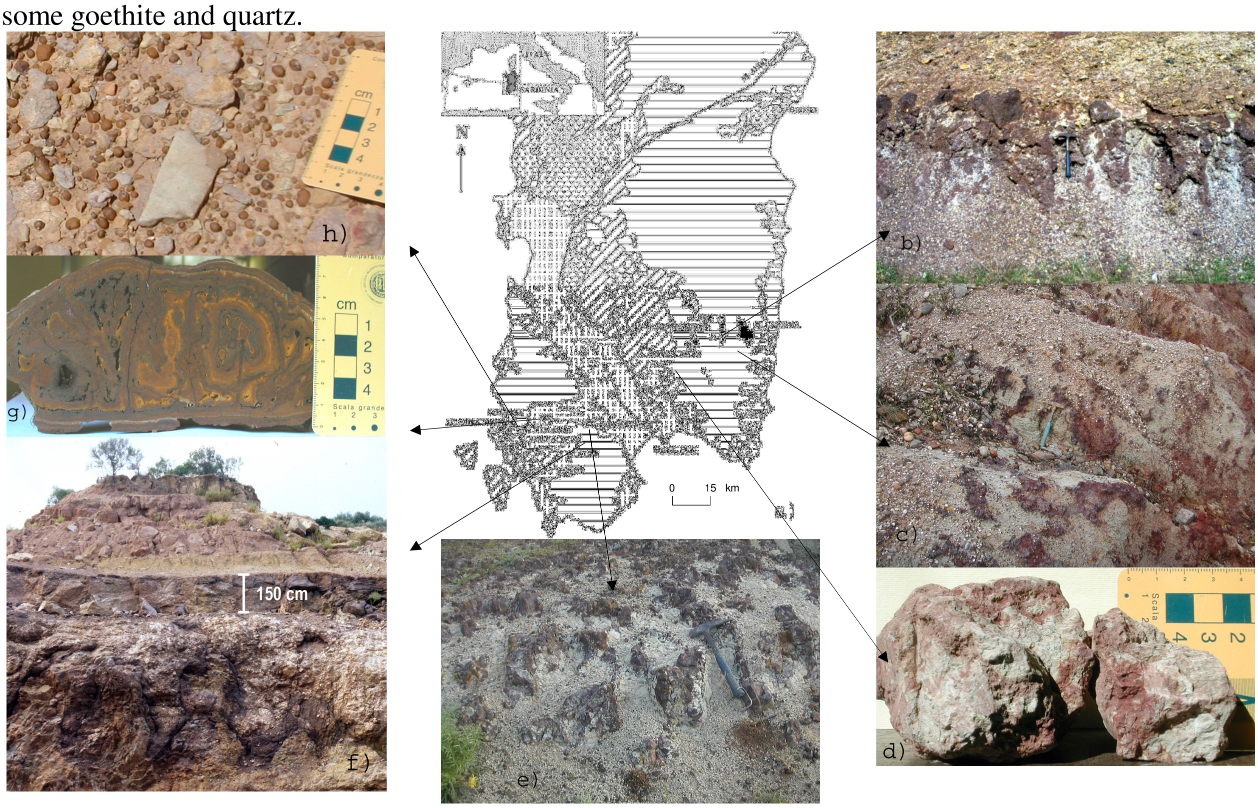


**Figure 1. a) Spatial distribution of the seven outcrops of Upper Cretaceous-Lower Paleocene ferruginous paleoalterites in Sardinia; b) Monte Maraconis outcrop; c) Ballao outcrop; d) fragments from the Sant'Andrea Frius outcrop; e) Villamassargia outcrop; f) Nuxis outcrop; g) large concentric ferruginous nodule from the Piolanas outcrop; h) pisolithic nodules from the Guardia Pisano outcrop.**

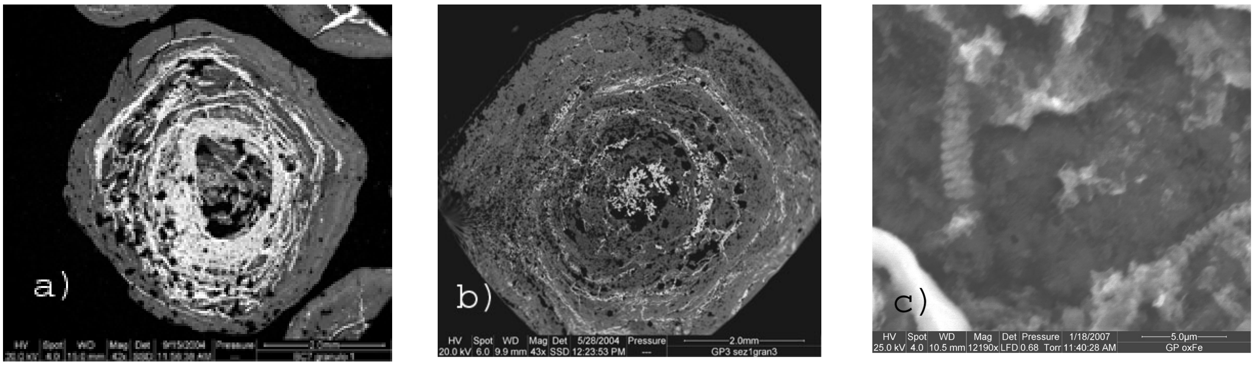


**Figure 2. SEM/EDS images of Nuxis (a) and Guardia Pisano (b) concretions showing the concentric distribution of their mineralogical components; c) SEM/EDS image of a Guardia Pisano concretion showing twisted stalks similar to the *Gallionella* ones.**

Traces of calcite are also present. The chemical composition is the following: $Fe_2O_3$ 27-24%, $Al_2O_3$ 21-19%, BaO 32-14%, and CaO 2.9-0.07%. At Piolanas, where the substrate is formed by Cambrian dolomitic metalimestones, large concentric ferruginous masses, which are made up of nodules soldered each others with growth, are found at the surface of a plowed soil, probably testifying for a former ironstone in the area (Figure 1g). The mineralogical analysis shows the presence of goethite and, subordinately, quartz and magnetite. At Guardia Pisano the basement is made up of Permian metaclaystones. The paleosol is represented by pisolithic levels in marly clays (Figure 1h), covered by Upper Paleocene-Lowermost Eocene shallow water marine sediments. The mineralogical analysis shows the presence of very abundant goethite in the pisoliths and very abundant calcite in the sediments. The chemical analyses show the same trend, with $Fe_2O_3$ contents of about 49% in the pisoliths and from 1 to 5% in the sediments and CaO content ranging from 32 to 43% in the sediments and from 1 to 4% in the pisoliths. SEM/EDS observations on the pisolithic concretions of Nuxis show the concentric distribution of their main mineralogical components (Figure 2a). The nucleus is made up by kaolinite and hematite. The cortex of the pisoliths is often thick and is made up of layers of hematite and kaolinite, alternating with the concentric planes of a complex system of craze planes filled by microcristalline barite precipitates. SEM/EDS observations on the pisolithic concretions of Guardia Pisano show a concentric primary structure starting from a kaolinitic nucleus (Figure 2b). The nucleus is covered by concentric layers of goethite, alternating with the concentric craze planes filled by microcristalline barite and calcite precipitates. The SEM images of the pisoliths support the hypothesis of bacterial contribution in the precipitation of iron hydroxides (Figure 2c).

The Maastrichtian ironstone outcropping near Marseille (southern France), studied by Saurel *et al*. (1976), is formed by pisolithic concretions, consisting of several concentric layers enveloped around quartz grains, mainly composed by $Fe_2O_3$ (56.2-33.8%), $Al_2O_3$ (11.5-8.5%), and CaO (12.3-0.8%). Kaolinite is the only clay mineral; among the Fe oxides, goethite prevails on hematite. In northern Aquitaine (south-western France) there are numerous outcrops of a pisolithic ironstone, lying on a Jurassic-Cretaceous karstified carbonate substrate and covered by Lower Eocene marine deposits. In the Montchoix outcrop, pisoliths, representing more than the 56% of the volume, are contained in clays lying on Campanian limestones and are covered by Cuisian marine clays (Gourdon-Platel 1980). The pisolithic concretions, formed around the K/T boundary, show a concentric distribution of their mineralogical components and contain large amounts of iron oxides (more than 60%), with goethite (70-80%) strongly prevailing on hematite, and low $Al_2O_3$ content (10-15%).

The main features of the ferruginous paleosols located at Monte Maraconis, Ballao, Sant'Andrea Frius and Villamassargia, as well as those of the two lowest horizons at Nuxis, indicate the presence of petroplinthic horizons (IUSS Working Group WRB, 2006). The large concentric ferruginous nodules soldered with growth found at the surface of a plowed soil at Piolanas may also be considered as part of a former petroplinthic horizon. The upper horizon at Nuxis fits the requirements for the pisoplinthic horizon (IUSS Working Group WRB, 2006) while the pisolithic levels at Guardia Pisano can be referred to a former pisoplinthite in the area. Pisoplinthic horizons are also present in the two considered French outcrops.
The genesis of these petroplinthic and pisoplinthic horizons may be related to the warm and humid tropical climatic conditions occurring during Latest Maastrichtian-Lower Paleocene (Danian), which favored the formation of plinthic horizons, followed by the increasing dry conditions occurring during the Paleocene, which favored the irreversible drying of the plinthic horizons in petroplinthic and pisoplinthic horizons. The

 
1 – 6 August 2010, Brisbane, Australia. Published on DVD.

formation of the pisoliths at Nuxis can be related to the presence of a ferruginous plasma, derived from the leaching of the underlying ferruginous deposits during more humid periods, that reorganized itself in concentric bands around nucleus of kaolinite and hematite. At Guardia Pisano, on a clayey substratum characterized by very slow drainage, the pisoliths could have formed similarly, but with goethite in state of hematite. In both cases, their regular structure tends to be obliterated during the repeated phases of hardening, drying and cracking as testified by the many craze planes. The precipitation of microcrystalline barite, leached from the barite-rich Paleozoic substrate, in the tensional planes opened in the pisoliths could have happened during and after their formation. Both in Sardinia and France (Gourdon-Platel, 1980), the bacterial contribution in the precipitation of iron hydroxides has been pointed out.

The constant stratigraphic position (around the K/T boundary), the large extent, and the supposed lateral continuity of the discussed ferruginous paleosols, of which the Sardinian and French outcrops are scattered remnants, are all important requirements to consider them as a pedostratigraphic unit (NACSN, 2005). According to the latest revision of NACSN (2005) the fundamental and only unit in pedostratigraphic classification is the geosol, which consists of a traceable, mappable three-dimensional body of soil material comprising one or more differentiated pedologic horizons (petroplinthic and pisoplinthic horizons, in the study area) (INQUA Working Group, 1995; Catt, 1998). As the physical and chemical properties of a specific pedostratigraphic unit may vary greatly, both vertically and laterally, from place to place (NACSN, 2005), a geosol is not a soil or paleosol, but rather a whole soilscape that can be recognised as a laterally extensive stratigraphic horizon (Morrison, 1978). The considered ferruginous paleosols clearly separates different sedimentary cycles and point to a period of relative geomorphic stability. For all these reasons, the paleosols at issue can be defined as a geosol.

## Conclusions

The numerous small outcrops, found in Sardinia and southern France, containing remnants of petro- and pisoplinthic horizons, have important implications for understanding climate regimes in the south-eastern margin of the European paleocontinent in the Late Cretaceous-Early Paleocene. The evidence they provide can be helpful in establishing extensive chronostratigraphic correlations as well as regional-scale morphostratigraphic correlations. Consequently, these outcrops represent a pedostratigraphic unit worthy of consideration in future regional geological mapping.

## References

Catt JA (1998) Report from working group on definitions used in paleopedology. *Quaternary International* **84**, 51-52.

Gourdon-Platel N (1980) Les cuirasses de fer pisolithique du tertiaire continental de la bordure Nord-Aquitaine: typologie des pisolithes et hypothèses sur leur formation. *Revue de Géomorphologie Dynamique* **4**, 129-142.

INQUA Working Group (1995) Definitions used in paleopedology. Paleopedology Glossary. 2nd Draft, July 1994. *INQUA/ISSS Paleopedology Commission, Newsletter* **11**(2), 35–37.

IUSS Working Group WRB (2006) World reference base for soil resources 2006. 2nd edition. World Soil Resources Reports n. 103. FAO, Rome.

Morrison RB (1978) Quaternary soil stratigraphy concepts, methods and problems. In 'Quaternary Soils' (Ed. WC Mahaney), pp. 77-108. (Geoabstracts, Norwich).

Murru M, Ferrara C, Matteucci R, Da Pelo S (2007a) I depositi carbonatici palustrini paleocenici della Sardegna centro-meridionale (Italia). *Geologica Romana* **40**, 201-213.

Murru M, Ferrara C, Matteucci R, Da Pelo S, Vacca A (2007b) I depositi continentali ferruginosi del Maastrichtiano sommitale-Paleocene della Sardegna meridionale (Italia). *Geologica Romana* **40**, 175-186.

NACSN (North American Commission on Stratigraphic Nomenclature) (2005) North American Stratigraphic Code. *American Association of Petroleum Geologists Bulletin* **89**(11), 1547-1591.

Saurel P, Arlhac P, Gouvernet C, Redondo C, Rousset C (1976) Présence d'une cuirasse gravillonaire ferrugineuse dans le Rognacien de Sénas (Bouches-du-Rhône, France). *Paléogéographie. Bulletin de la Société Géologique de France* **18**, 59-67.