

## **PS Economic Impact of Carbonates Formed under Continental Conditions\***

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### **Abstract**

Non-marine carbonates are very valuable geological resources that appear extensively represented in a wide range of depositional environments: lacustrine, palustrine, calcretes, etc. In the same manner, carbonates that undergo alteration processes under continental conditions have as well great importance from an economic point of view. Their economic usefulness is determined by their physical properties and chemical composition. Lacustrine and palustrine carbonates and their associated deposits are both source and reservoir rocks of petroleum; they may host coal and oil shale, and may contain valuable industrial minerals and rocks such as sepiolite, palygorskite, sodium carbonates, etc. These rocks are also broadly used for less added value applications like aggregates, cement manufacture, building stone, etc. Calcretes have proven to be great geochemical tracers for gold exploration and appear as great host rocks of uranium deposits. Other carbonate phases formed under continental conditions are deposits of HDT (hydrothermal dolomite). These deposits are proved to be associated to mineral resources as Mississippi Valley type mineralizations. The presence of this type of alteration has a major impact on hydrocarbon reservoir type, geometry, quality and distribution.

Herein we describe some of those deposits by discussing the geological setting conditions where the resource is formed, the processes involved in their origin and the major factors controlling their formation. Examples of case studies of different resources permit to understand the economic significance of these economically important deposits.

# ECONOMIC IMPACT OF CARBONATES FORMED UNDER CONTINENTAL CONDITIONS

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## RESOURCES RELATED TO LACUSTRINE AND PALUSTRINE ENVIRONMENTS

### Oil and gas reservoirs in lacustrine rocks

Lacustrine rocks may act as a source or as a reservoir of hydrocarbons. In many continental rift basins, lacustrine shales and marls are significant source rocks (Fig. 1). Lacustrine deposits are important oil source rocks in rift basins in Southeast Asia, West Africa and Brazil. In Brazil, up to 85% of oil source rocks are regarded as lacustrine in origin. This is, for instance, the case of the Campos Basin petroleum system in southeastern Brazil, the source rock of which can be found in the lacustrine shales and marls of the Lagoa Feia Formation. The calcareous black shales of this formation were deposited in lake systems that occupied rift basins formed during plate separation during the Early Cretaceous (Barremian rift phase). The Lagoa Feia source rocks reached maturity in parts of the Campos Basin during the Miocene as a result of the deposition of several thousands of metres of Tertiary clastic sediments.

More than 20 billion barrels of oil have been produced from 400 different fields in lacustrine basins in China, Indonesia, Thailand, Vietnam and Malaysia. Some of these fields, such as Daqing (China), Minas (Indonesia) and Bach Ho (Vietnam), are designated giant oil fields. In China, more than 95% of reserves are considered to be of lacustrine origin. The Songliao Basin, covering an area of 250,000 km<sup>2</sup>, is known as one of the world's most prolific oil- and gas-producing basins. In the Kambalia Field of Angola, oil and gas are obtained from the lacustrine Toca carbonate facies (Barremian to Aptian). The deposition of the reservoir, the Toca carbonate, occurred during the continental rifting in the early history of the Lower Congo Basin prior to complete opening of the south Atlantic. Depositional systems consisted of interconnected lakes that were fringed by algal, oncotic and marl carbonates or sandy lacustrine shorelines.



Figure 1.- Lower Cretaceous Leza Formation (La Rioja, Spain): lacustrine limestones, dolostones and marls (Courtesy of Javier Hernán).

### Coal from carbonate-rich lacustrine systems

Significant coal deposits (Fig. 2) occur in carbonate-rich lacustrine successions in Greece. Greek lignite deposits formed during the Pliocene and Pleistocene in shallow lakes and marshes of closed intermontane basins. The Kozane-Ptolemais-Amfiteo-Florina Basins in Macedonia contain most (about 64%) of the national coal resources. The Miocene Mugla Basin in Turkey is one of the most productive lignite basins. Coal deposits embedded in lacustrine carbonates form part of the Miocene Sekköy and Millet Formations and formed during the highstand phase of the lake level. Their origin is linked to the development of peatlands in carbonate-rich lacustrine environment during periods of low detrital supply.



Figure 2.- Coal mine in Espiel (Córdoba, Spain).

### Sepiolite and palygorskite in lacustrine and palustrine carbonates

Sepiolite and palygorskite are magnesium-rich, fibrous argillaceous minerals. They occur in lacustrine, palustrine and calcareous deposits formed either by direct chemical precipitation or as a result of diagenetic processes. Based on its absorption properties, sepiolite and palygorskite are used to purify petroleum products such as lubricating oils and transformer oils, in the manufacture of white copy paper, in domestic and urban liquid sewage treatment, to separate gases and vapours including hydrocarbons and at least one fault zone. The manufacture of refractory and ceramic elements and electrical insulators, in pharmaceutical and cosmetic products, paints, inks and polishes, oil-well drilling and for domestic use as cat litter.

Examples of lacustrine deposits containing palygorskite and sepiolite include the Late Oligocene of the southeastern United States, the Amargosa desert in Nevada, Anatolia, Turkey and the Jordan Valley. Deposits of palustrine character that contain sepiolite are documented from the Miocene deposits of the Madrid Basin in Paracuellos de Jarama (Fig. 3). Near Madrid, the Vicalvaro quarry is the world's largest sepiolite reserve. This quarry occupies an area of 7.5 km<sup>2</sup> and the maximum thickness of the sepiolite-bearing deposits is 35m in the central area.



Figure 3.- Sepiolite quarry (Barajas, Spain), with an alternation of sepiolite, marls and clays. (Courtesy of M. Bustillo).

### Palustrine carbonates used in construction

In addition to the use as ornamental stone (Fig. 4), one of the main uses of carbonate rocks is in the manufacture of portland cement, both as components of the raw mix and as supplements to the final product. Cement consumption has increased over the decades and continues to grow due to the rise in population and need for construction materials. A good example of a continental carbonate deposit used to manufacture cement is the Late Miocene Caliza del Páramo Formation in the Madrid Basin (Spain). This unit is the source material for four cement factories with annual limestone consumption of about 10 million tons and a total production capacity of 6.5 million tons per year of clinker. In this area, the Caliza del Páramo Formation (Fig. 5) is represented by a 15 m-thick succession of lacustrine marls, with a 1.5-2 m. thick level showing clear evidence of its palustrine nature; it contains small lenticular pseudomorphs of gypsum, desiccation cracks and fenestral facies.



Figure 4.- Palustrine limestone used as ornamental stone (Madrid, Spain).



Figure 5.- Palustrine limestone quarry. It feeds more than two million tons per year to Lafarge's Villaluenga cement works.

## INTRODUCTION

Non-marine carbonates are very valuable geological resources that appear extensively represented in a wide range of depositional environments: lacustrine, palustrine, calcaretes, etc. In the same manner, carbonates that undergo alteration processes under continental conditions have as well great importance from an economic point of view. Their physical properties and chemical composition determines their economic usefulness and importance. Lacustrine and palustrine carbonates and their associated deposits are both source and reservoir rocks of petroleum, they may host coal and oil shales, and may contain valuable industrial minerals and rocks such as sepiolite, palygorskite, sodium carbonates, etc. These rocks are also broadly used for less added value applications like aggregates, cement manufacture, building stone, etc.

Calcretes have proven to be great geochemical tracers for gold exploration and appear as great host rocks of uranium deposits. Other carbonate phases formed under continental conditions are deposits of HDT (hydrothermal dolomite). These deposits are proved to be associated to mineral resources as Mississippi Valley type mineralizations. The presence of this type of alteration has a major impact on hydrocarbon reservoir type, geometry, quality and distribution.

Herein we present some deposits associated to continental carbonates and deposits formed under continental conditions by discussing the geological setting conditions where the resource is formed, the processes involved in their origin and the major factors controlling their formation.

### Lacustrine and Palustrine

Lacustrine sediments are composed of mudstones, marls, limestones and sandstones. Subaerial exposure of calcareous lacustrine muds and fluctuations in the water table lead to the formation of palustrine limestones. Climate, bedrock composition and topography of the catchment area have been proposed as major controlling factors of the quality of source rocks due to their effects on nutrient availability and water chemistry. High organic productivity levels and preservation potential and low matrix sedimentation rates maximize the source rock potential of a lacustrine rock.

Lacustrine and palustrine carbonates and their associated deposits are both source and reservoir rocks of petroleum; they may host coals and oil shales, and may contain industrial minerals such as sepiolite and palygorskite, as well as materials used for construction.

### Carbonates formed by alteration under continental conditions

The term "karst" refers to geomorphological features formed when carbonate rocks are dissolved by meteoric waters. Karst developed on carbonate rocks covers and underlies large areas of the ice-free continental region of the Earth, and roughly 20-25% of the world population depends largely or entirely on groundwater obtained from karst reservoirs. The dissolution of carbonate rocks by groundwater during their subaerial exposure is an important geological phenomenon that leads to the formation of "secondary" continental carbonate deposits such as bauxite or caves where water or hydrocarbons may accumulate.

Magnesite deposits are other example of carbonates formed under continental conditions. When formed in sedimentary conditions, magnesite is always considered a secondary carbonate and typical product of advanced diagenesis related to hydrothermal fluid circulation.

### Karst and petroleum reservoirs

Hydrocarbons occur in all the different types of karsts, and show a mutually exclusive relationship with the presence of bauxite. Karst related reservoirs are commonly very heterogeneous, hindering the search for oil and gas. During karstification, ground and subsurface waters that are undersaturated in carbonate minerals dissolve carbonate rocks and create an abundantly vuggy pore space. As dissolution continues, the vuggy pore space may widen to form large cavities, causing the overlying rocks to collapse and form karst breccias. Following dissolution, the pore space may be filled by mineral precipitates. These processes also occur at a megascale and form reservoirs at the scale of caves. An example of this type of oil reservoir is the Mississippian Madison reservoir of the Elk Basin field in Wyoming. The Madison carbonate succession was subjected to significant dissolution by groundwater, which removed the more soluble limestone but left the less soluble dolomite, forming abundant secondary porosity.

### Aquifers in karst systems

The hydrology of karst aquifers has attracted much interest since early historic times with caves serving as water-carrying pathways. Karst aquifers can be distinguished from aquifers in non-karst rocks by the presence of conduits that act as rapid through pathways carrying water from sinking streams and sinkhole inputs to springs. The formation of aquifers is the same as described for oil reservoirs, that is, ground and subsurface waters dissolve carbonate rocks and create pore spaces at different scales, the porosity being in this case filled with water.

In Spain, karst aquifers contain renewable water resources of some 15 km<sup>3</sup> per year, of which about 1.7 km<sup>3</sup> is extracted each year. Approximately 29% of the surface of peninsular Spain is formed by carbonate and evaporite rocks that undergo karstic processes. Many rivers in Spain are sourced by springs in karst terrains (Fig. 9), and the waters from such springs are used for widely varying purposes, including urban supply, irrigation, industry, bottling plants and health spas. Other examples of karstic aquifers are found in North America in the states of Indiana, Kentucky, Tennessee, Illinois and Virginia. Most karst in the eastern United States developed on limestone generating fluvio-karst landscapes.



Figure 9.- The river Mundo's spring (Albacete, Spain), fed by the Calar del Mundo karstic system.

## TRAVERTINES AND TUFAS AS ECONOMIC RESOURCES

### Travertine as building and ornamental stone

Central Italy harbours more than 100 travertine outcrops all younger than 400 ka, and in some places travertine precipitation continues, especially around active geothermal areas. Travertine has been used widely as a building stone. The Romans used it for both structural and decorative material for buildings and bridges. Late Pleistocene travertines up to 40m thick near Rapolano Terme in Tuscany, central Italy, were precipitated by hot water issuing from springs on hillsides and flowing into adjacent depressions to mix with rainwater. These Tuscan travertines have been quarried intensively for ornamental and building stone (Fig. 10 and 11) and range in age from Late Pleistocene to the present. The quarried level (Late Pleistocene-Early Holocene) covers an area of 14 km<sup>2</sup>, is up to 40m thick and harbours two quarries.

Travertine was one of ancient Egypt's most popular ornamental stones. Egyptian travertine has a dense, non-porous character that is described as "calcareous sinter". Egyptian travertine deposits were the result of carbonate precipitated from hydrothermal fluids associated with the Red Sea Rift in the Oligocene.



Figure 10.- Travertine used for construction. Coliseum (Rome, Italy).



Figure 11.- Travertine column in Rome's Foro (courtesy of A. Alonso).

### Travertine and tourism

The spectacular geomorphology of some travertines makes them important tourism sites. Mammoth Hot Springs, near the northern boundary of Yellowstone National Park, Wyoming, USA, is one of the world's largest areas of active travertine precipitation and is one of the most famous tourist sites in North America. The travertine deposits at Mammoth Hot Springs are approximately 8,000 years old. The travertine is 73m thick and includes more than 4 km<sup>2</sup> of terraced travertine forms and fissure-ridge deposits, among which the terraces are the volumetrically dominant morphology.

Another site of tourist interest is the Pamukkale deposits, locally called "Cotton Castle", in the West Anatolian sector of the Aegean extensional province of Turkey. The name refers to the snow-white travertines that continue to be deposited. Travertine deposition at Pamukkale, one of Turkey's most visited tourist destinations, has been in progress over at least the last 400,000 years. The travertines form from hot waters that emerge at 35-50°C from open fissures and at least one fault zone. The total area occupied by the modern and ancient travertines is more than 100 km<sup>2</sup> and the thickness can reach 60m.

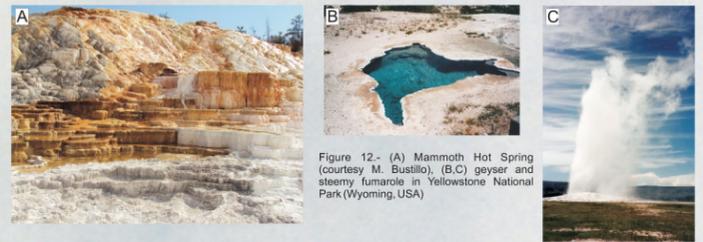


Figure 12.- (A) Mammoth Hot Spring (courtesy M. Bustillo), (B,C) geyser and steam fumarole in Yellowstone National Park (Wyoming, USA).

### Tufa as building material

Tufas have been extensively employed in Europe since the Middle Age in building, especially in big public buildings. The low density of this material makes it very interesting for the upper parts of high buildings like cathedrals, palaces, etc. In order to avoid the overload of the structure.

One example is the Cifuentes Church (Guadalajara, Spain) that has the upper part of the walls made with tufa (Fig. 13).



Figure 13.- Cifuentes Church (A) built with tufa and close up of the upper part of the wall (B). (Cifuentes, Guadalajara, Spain).

## CALCRETES

### Gold-bearing calcretes

Calcretes have proven to be significant geochemical tracers for gold exploration in Australia, Mexico and South Africa. Concentrations of gold in calcretes generally are very low, typically between 0.5 and 500 parts per billion (ppb), but it appears to have a strong correlation with calcium concentrations in calcretes that form over gold ore bodies. Gold appears diluted in the calcrete as a result of plant-derived infiltration and evapotranspiration of meteoric waters. Models for the accumulation of gold in calcretes propose a geomicrobial pathway for the co-precipitation of calcium and gold in semi-arid zones. As calcrete develops over a gold-rich substrate, gold may be dissolved by organic acids and reprecipitated together with CaCO<sub>3</sub>. An example of this is the Challenger Gold Deposits in the northern Gawler Craton which is found 750 km NW of Adelaide (southern Australia). It was discovered in 1995 as the direct result of calcrete sampling. Calcrete appears across most of southern Australia as a variable hardpan horizon up to 2m thick just beneath the surface, where a broad gold anomaly (>5 ppb across an area of over 4 km<sup>2</sup>) occurs in the calcrete overlying the Challenger ore body.



Figure 14.- Field example of a calcrete horizon with roots and motting.

### Calcretes and uranium deposits

The various types of uranium ores include surficial deposits, which are broadly defined as young (Tertiary to modern), near-surface uranium concentrations in sediments or soils. Uranium mineralization occurs in fine-grained surficial sands and clays, cemented by calcium and magnesium carbonates. Surficial deposits comprise about 4% of the world's uranium reserves. Uranium deposits in calcrete are the largest of the surficial deposits. Calcrete deposits related to uranium ores in Australia form in places where uranium-rich granites are deeply weathered in a semi-arid to arid climate. The Yerrinton deposit in western Australia is by far the world's largest surficial deposit. Calcrete uranium deposits also occur in the Central Namib Desert of Namibia (Rossing area). Namibia's identified uranium resources account for some 5% of the world's known total. The recoverable reserves are estimated at about 275,000 tons of uranium.

### Calcretes as building stone

Calcretes are also used as aggregate, construction material and building stones. The key properties of calcretes that determine their usefulness as aggregates include: natural moisture content, bulk density, liquid limit, plastic limit and grain-size distribution. The natural moisture content and field density of calcrete depend on the intensity of calcareization and the nature of the calcareized source sediments. In the Unified Soil Classification scheme, calcrete aggregates are grouped under the classes gravel and sand.

In the Thar Desert in India, where traditional road-paving aggregates are scarce, calcretes have been used as aggregate for low-cost road construction. A variety of calcretes and ferrocetes were formed by the weathering of dune sands and rock masses and are associated with dunes, interdune alluviums and pediments.

## Conclusions

Continental carbonate resources appear in every corner of the world, in Europe, North and South America, Africa and Asia. Since ancient times, continental carbonates have proven to be sources of energy resources, such as petroleum, gas, uranium and coal; metals and industrial minerals, such as gold, bauxite, palygorskite, sepiolite and diatomites; water in numerous regions in the world; and raw materials for construction, including the manufacture of concrete or aggregate, and travertine for construction and ornamental rocks.

The main geological factors that control the occurrence of the different resources in continental carbonates are climate, bedrock composition, topography and the geological and tectonic setting. Climate is intimately related to changes in the base-level of lakes, acidity (a key factor for the formation of sepiolite and palygorskite) and the quantity and composition of meteoric water (important for karst development), and controls plant communities (which control soil deposition). The composition of the host rock and bedrock in the catchment area is the major factor controlling the formation of a resource. The dissolution and leaching of the host rock provides the cations needed to form the various resources (sepiolite-palygorskite, travertines, calcretes, bauxites, etc.). Similarly, the rock and mineral contents of catchment areas also have significant effects on the availability of nutrients and water properties which are important for lacustrine environments, and the possible formation of travertine and karst forms.

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## RESOURCES RELATED TO CARBONATES TRANSFORMED UNDER CONTINENTAL CONDITIONS

### Hydrothermal dolomites and magnesite

Magnesite is a major source of MgO for basic refractory lining of furnaces in the iron and steel industry, and also for building, chemical, electrical and livestock feed industries, as well as the growing field of magnesium metal production. Magnesite deposits of hydrothermal origin appear associated to HDT (hydrothermal dolomite) in several quarries in Spain. The establishment of the factors and mechanism that control the diagenetic evolution of these carbonates has a great importance in order to understand and predicts porosity and permeability variations of rocks formed under similar geological conditions.

### Bauxites and carbonate karst

Bauxite is the primary ore of aluminium, composed mainly of aluminium oxide and hydroxide minerals. Bauxites have a range of commercial applications such as the production of aluminium metal and aluminium-based chemicals, abrasives, cements and refractory materials. Major bauxite deposits are formed at advanced stages of the development of weathering profiles in tropical, coastal, mountain or plateau karst environments. Bauxite formation may be related to multiple and single unconformities as well as to calcretes.

Jamaica is a major exporter of aluminium ore. In Jamaica, bauxites form either as soil layers mantling an extensive limestone horizon or as masses tens of metres thick in sinkholes and solution cavities in well-developed karst topography.

Bauxite deposits in karst appear also in the Taurides region of Turkey. The most important bauxite deposits, Dogankuzu and Morlas, are karst-related, unconformity-type deposits in Late Cretaceous platform limestones and shales that formed in a passive margin setting of the Tethys Ocean. The closure of the ocean as well as local uplift of the passive margin led to a relative sea-level fall that resulted in karstification and bauxite formation in topographic lows, as represented by the Dogankuzu and Morlas deposits. The ore thickness varies from 1 to 40 m. An in-depth survey identified, in the Morlas area, a 57% Al<sub>2</sub>O<sub>3</sub>.

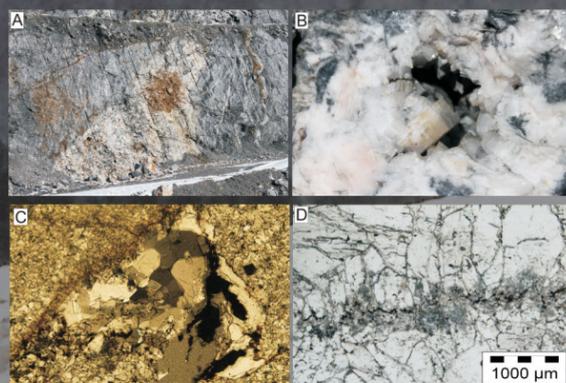


Figure 6.- (A) Eguiluz magnesite quarry (NE Spain). Magnesite was formed by hydrothermal fluid circulation through fracturing and stylolite planes. (B) HDT dolomite crystals filling vug voids. (C) Thin section of a magnesite sample with a void filled by HDT. (D) Thin section photograph showing the magnesite crystal growing from a stylolite plane.

### Karst caves and tourism

Many protected natural spaces of great value occur in karstic areas (exokarst enclaves and karstic cavities). Some caves are developed for tourist use, and receive millions of visitors every year. Thus, they make a significant contribution to the development of rural areas and provide important economic benefits for the areas in which these caves appear. In some cases, caves contain important elements of natural and cultural heritage, such as archaeological sites, sometimes in the form of rock paintings.



Figure 8.- Guilin's region Karst, one of the most visited areas of China. (Courtesy of R. Gries).