Liesegang rings in pelagic limestones: genetic considerations

Estructuras Liesegang en calizas pelágicas: consideraciones genéticas

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ABSTRACT

Liesegang rings have been recognized in Middle Jurassic pelagic marly limestones of the Subbetic, Southern Spain. The rings of these structures consist of iron hydroxide concentrations and/or small textural changes and are three-dimensionally distributed in the limestone and marly limestone beds. These structures have been previously described in siliceous rocks, in volcanic rocks and only rarely in limestones and marls. Liesegang rings are the result of geochemical and textural self-organization processes mainly produced by iron-rich fluids coming possibly from contemporaneous volcanic rocks. Chemical, mineralogical and textural changes occurred prior to the lithification of the marly limestone beds, as is demonstrated by the presence of synsedimentary faults affecting these structures.
Key words: Liesegang rings, limestone, pelagic, Jurassic, Subbetic

RESUMEN

Se estudian estructuras Liesegang que aparecen en calizas margosas pelágicas del Jurásico Medio del Subbético, sur de España. Los anillos de estas estructuras consisten en concentraciones de hidróxidos de hierro y/o pequeños cambios texturales y están distribuidos tridimensionalmente en los lechos de calizas y de calizas margosas. Estas estructuras han sido descritas previamente en rocas silíceas, en rocas volcánicas y sólo raramente en calizas y margas. Las estructuras Liesegang son el resultado de procesos de auto-organización geoquímica y textural, producidos principalmente por fluidos ricos en hierro procedentes posiblemente de rocas volcánicas contemporáneas. Los cambios químicos, mineralógicos y texturales tuvieron lugar antes de la litificación de los lechos de calizas margosas, como lo demuestra la presencia de fallas sinsedimentarias que afectan a estas estructuras.

Key words: *Liesegang, pelagic, Limestones, Jurassic, Subbetic.*

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Introduction

The Liesegang phenomenon is one of the most frequently studied examples of rhythmic precipitate formation in gels (Henisch, 1988). It consists of "intermittent precipitation that occurs when two reacting solutions at concentrations far from stoichiometry are allowed to counterdiffuse" (García-Ruiz *et al.*, 1996). The Liesegang phenomenon most commonly comprises bands or rings with a three-dimensional network, known as Liesengang rings (Carl and Amstutz 1958; Henish and García-Ruiz, 1986a,b; Henish 1988, 1991; Kuo *et al.*, 1997), Liesegang bands (Krug *et al.*, 1996), Liesegang structures (Büki *et al.*, 1995a), or Liesegang patterns (Chopard *et al.*, 1994a,b) in recognition of R.E. Liesegang, who first described and obtained in the laboratory these structures (Liesegang, 1913).

In addition to Liesegang's pioneering work, these structures have been obtained in more recent experimental simulations in the laboratory (Krug *et al.*, 1996; López-Cabarcos *et al.*, 1996; Moxon, 1996; García-Ruiz *et al.*, 1996; Kuo *et al.*, 1997). Liesegang rings have been recognized in sedimentary rocks, mainly in siliceous varieties (Bustillo and Martín-Escorza, 1984; Landmesser, 1988; Chang and Yortsos, 1994; Heaney and Davis, 1995; Moxon, 1996; Shahabpour, 1998) and in volcanic rocks (Carl and Amstutz, 1956; Cooper *et al.*, 1996; Toramaru *et al.*, 1997). Gindy *et al.* (1985) studied spheroidal weathering in marls and chalks that they interpreted as initiated by Liesegang diffusion. Ortoleva (1994a,b) described repetitive mineralogic patterns in limestone/marl alternations ascribed to Liesegang rings.

In this paper Liesegang rings in pelagic limestones of the Middle Jurassic from the Subbetic are studied. Detailed observations of the sedimentary, stratigraphic and structural features of the carbonate rocks containing the Liesegang rings have revealed interesting aspects regarding their genesis.

Geographical and geological setting

The study area is located 8 km southwest of the village of Montillana (Granada province). The sites can be reached by the local agricultural road connecting the villages of Montillana and Trujillos (Fig. 1A), near of Puerto de la Taza and Cortijo Abejanar. Liesegang rings in pelagic limestones (or marly limestones) and in chert nodules in other localities in the Subbetic (e.g., Sierra de San Pedro and Cortijo de Almendralejo), with similar ages and geological context have also been recognized.

In these localities Liesegang rings appear in limestones and marly limestones interbedded in submarine volcanic rocks with pillow lavas. The limestones and marly li-

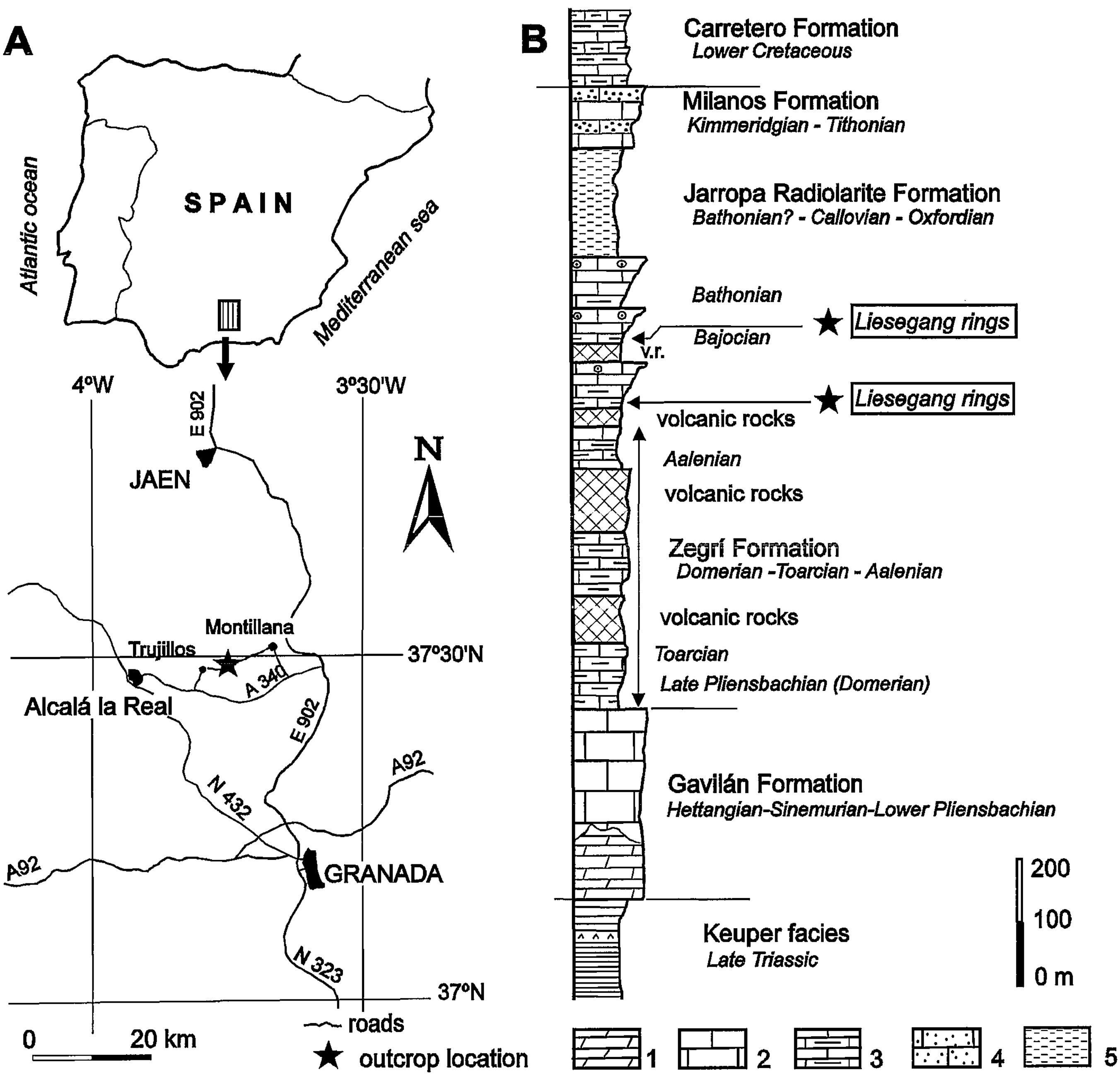

Fig. 1.- Location of the study site with Liesegang rings, southern Spain. 1A.- Geographical location of the most significant outcrop. 1B.- Stratigraphical section of the Jurasssic from Median Subbetic in the sectors with volcanic submarine rocks. Key: 1.- Dolomites; 2.- Limestones; 3.- Pelagic marls and marly limestones; 4.- Calcisiltites; 5.- Marly radiolarites.

Fig. 1.- Localización de los afloramientos estudiados con anillos de Liesegang, sur de España. 1A.- Localización geográfica del afloramiento más importante. 2.- Sección estratigráfica del Jurásico del Subbético Medio en los sectores con rocas volcánicas submarinas. Leyenda: 1.- Dolomías; 2.- Calizas; 3.- Margas y calizas margosas pelágicas; 4.- Calcilimolitas; 5.- Radiolaritas margosas.

mestones contain Aalenian and Bajocian ammonites and show intercalations of calcisiltites in which the dominant structure is horizontal lamination. These sediments were deposited along the Southern Iberian Continental Margin. The Mesozoic and Tertiary sediments deposited on this continental margin were tectonically deformed during the Middle Miocene as a consequence of the westward drift of the Alboran Microplate (Sanz de Galdeano and Vera, 1992).

These deformed Mesozoic-Tertiary sediments crop out in Southern Spain, where there are several geological units (Prebetic and Subbetic, and subdivisions in these) (García-Hernández *et al.*,1980; Vera, 1988). The Jurassic sedimentary rocks studied belong to the Median Subetic, a geological unit in the Subbetic characterized mainly by the presence of submarine volcanic rocks (with pillow lavas) that are interbedded with Middle Jurassic pelagic sediments (Fig. 1B). On the volcanic edifices, isolated carbonate platforms with oolitic limestones locally developed, that were interpreted as guyots (Vera *et al.,* 1997). In the Median Subbetic, Jurassic shallowing-upward cycles have been recognized, indicating a moderate depositional bathymetry for the pelagic sediments, including radiolarites and related facies (Vera and Molina, 1998; Molina *et al.,* 1999).

Liesegang rings

Liesegang rings in the Median Subbetic appear in limestones and marly limestones within a limestone/marl rhythmite. The carbonate rocks are mainly micrites (mudstone) with ammonites, sections of bivalves ("filaments"), crinoids, brachiopods, radiolaria, *Zoophycos* and *Chondrites*, all indicating that these sedimentary rocks were deposited in a marine pelagic environment at moderate paleodepth. The specific and/or generic classification of the ammonites indicate Aalenian and Bajocian ages for these rocks.

The carbonate beds with Liesegang are part of the sedimentary intercalations that lie between successive flows of submarine volcanic rocks. The best examples of Liesegang are found in the marly limestone beds adjacent to the volcanic flows, specially in the twenty metres directly overlying or underlying the volcanic rocks.

Geometric parameters

The most abundant geometric pattern for the Liesegang features is a series of bands or rings, that are three-dimensionally distributed within the limestone or marly limestone beds. The most frequent varieties are those enriched in iron hydroxide (Figs. 2A,C,D), giving the rings a yellow to orange colour. In other cases the bands of rings are marked by a slight textural change (with no significant change in colour) corresponding to a small increase in carbonate grain size (Figs. 2B,E), in which the coarse-grained rings have a greater abundance of peloids.

In both cases, there is commonly a difference in the intensity of recent weathering in rings, which enhances the visibility of these three-dimensional structures. The distances between adjacent bands of rings ranges from 1 mm to 2 cm, with geometric patterns very similar to those obtained experimentally (Carl and Amstutz, 1958; Krug *et al.*, 1996; Kuo *et al.*, 1997) and produced via computer simulations (Büki *et al.*, 1995a,b; Chopard *et al.*, 1994a,b).

At the outcrop scale, the geometry of the Liesegang rings is characterized by the local presence of a sub-spherical nucleus (Figs. 2B,D), with concentric rings progressively changing outward to more irregular forms.

Host rocks

The host rocks of the Liesegang rings are limestone/marl rhythmites. The limestones or marly limestone beds range from 10 cm to 90 cm thick, with an average of about 50 cm. Cherts appear in numerous carbonate beds, mainly forming small nodules with their largest dimension fequently parallel to the stratification. $CaCO_3$ content of marly limestones ranges between 68 % and 83 %. The insoluble residues in these beds are composed mainly of clay minerals. Quartz and iron hydroxides are the minor minerals. Liesegang rings in these limestone/marl rhythmites are marked by changes in colour due to the presence of iron hydroxides.

Some calcisiltites occur as interbeds within the limestone/marl rhythmite. The calcisiltite layers are 30-80 cm thick and show horizontal lamination quite frequently. Some calcisiltite layers also have small-scale cross-bedding, wave ripples lamination and hummocky cross-stratification. Liesegang rings in these calcisiltite layers are marked by iron hydroxide in content variations and/or slight textural changes, mainly in carbonate grain size. It can also be clearly seen how the Liesegang rings are superimposed to the primary internal sedimentary structures with no apparent correspondence.

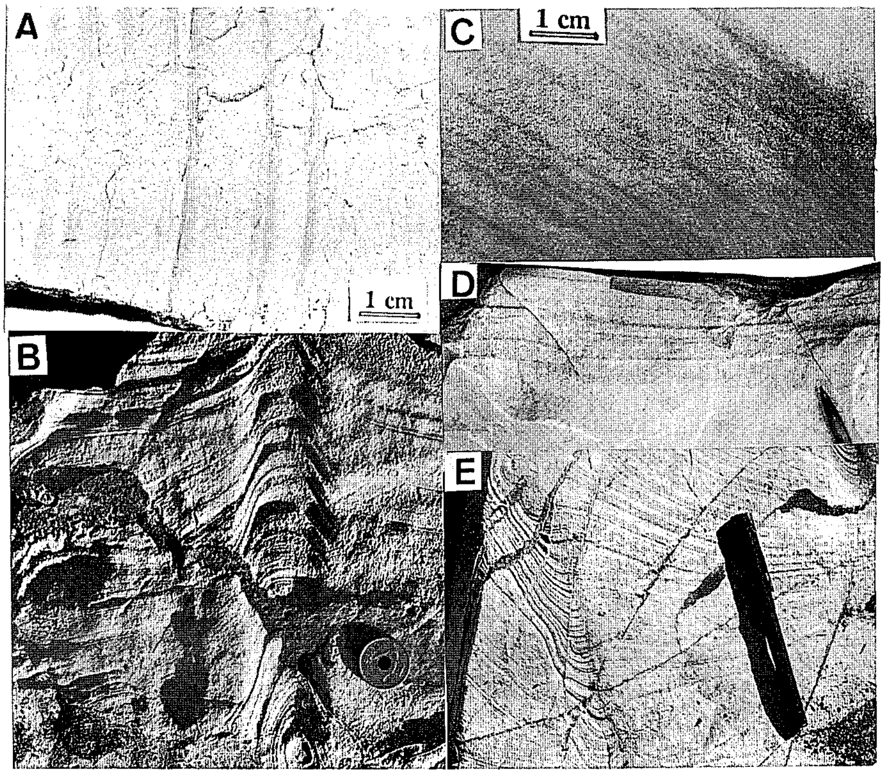

Fig. 2.- Photographs of Liesegang rings. A.- Concentric rings of iron hydroxides in marly limestone; B.- Liesegang rings in calcisiltite bed marked by slight textural changes. Coin is 2 cm in diameter; C.- Concentric rings of iron hydroxides in marly limestone with typical Liesegang pattern; D.- Synsedimentary faults affecting Liesegang rings. Pencil is 1 cm wide. E.- Liesegang rings in calcisiltite bed marked by slight texture changes and small synsedimentary faults. Pencil is 13 cm long.

Fig. 2.- Fotografías de estructuras Liesegang. A.- Anillos concéntricos de hidróxidos de hierro en caliza margosa; B.- Anillos de Liesegang en nivel calcilimolítico marcado por ligeros cambios texturales. La moneda tiene un diámetro de 2 cm; C.- Anillos concéntricos de hidróxidos de hierro en caliza margosa con modelo típico de Liesegang; D.- Fallas sinsedimentarias afectando a los anillos de Liesegang. El lápiz tiene 1 cm de ancho. E.- Anillos de Liesegang en lecho calcilimolítico marcado por ligeros cambios texturales y pequeñas fallas sinsedimentarias. El lápiz tiene 13 cm de longitud.

Synsedimentary features

In the limestone and marly limestone beds there are frequent synsedimentary faults, which are particularly visible in the laminated intervals. They are small normal faults with a displacement generally under 2 cm, dissapearing at the top of the bed. The Liesegang rings are offset by these synsedimentary faults (Fig. 2C), indicating that they formed later than the sedimentation but prior to the synsedimentary faulting. There are also abundant examples of Liesegang rings in carbonate layers (limestones and marly limestones) without synsedimentary faults. Consequently, we can think that both phenomena are not genetically related.

At the base of some calcisiltite beds there are flame structures ranging from 5 mm to 3 cm in width and in height. They comprise flame-shaped plumes of micritic limestones squeezed irregularly upward into the overlying calcisiltite layer. These structures also represent synsedimentary features, very possibly coeval with synsedimentary faulting.

Discussion and genesis

The genetic relationship of the Liesegang rings with the sedimentation, diagenesis and weathering can be grouped into the following types: 1) penecontemporaneous with the sedimentation, 2) late diagenetic, and 3) the result of recent weathering. Examples of Liesegang rings genetically related to recent weathering are reported in the literature (Gindy *et al.*, 1985; Shahabpour, 1998). In our examples, however, this interpretation can be rejected since the rings appear not only on the weathered surfaces, but also on fresh surfaces, made with the hammer and in excavations produced during road building. It is significant that the Liesegang rings are affected by other synsedimentary structures, specially by synsedimentary faults. This demonstrates that the Liesegang rings were generated penecontemporaneously with the sedimentation, after deposition of limestone beds, but before the synsedimentary faulting.

A second aspect to be considered in this discussion is the genesis of the rings and the particular genetic conditions in which they may have been originated. The formation of Liesegang patterns has been investigated by many researchers, both from an experimental and a theoretical points of view. Several mechanisms have been proposed as the main genetic factor, but the supersaturation models based on Ostwald's ideas are possibly the most widely accepted (Ortoleva, 1994a; Chopard *et al.*, 1994a,b; Büki *et al.*, 1995a,b; Krug *et al.*, 1996). Liesegang rings are formed by interdiffusion of two chemical components. Once concentration of the two important species become high enough, nucleation occurs (this typically takes place at supersaturation well above equillibrium). With the continued growth of the precipitating phase, however, the local solution chemistry begins to approach the equilibrium state more closely. The banding or periodicity of the Liesegang phenomena, then, is related to the fact that crystal growth in the vicinity of developing bands reduces the solution saturation state below the nucleation barrier.

In our case we must assume that the two chemical components are: a) solutions with low oxygen conditions where Fe^{+2} is dominant, coming from volcanic edifices, and b) the diffused oxygen in the saturated groundwater. Products of intermitent precipitation were iron hydroxides, forming the Liesegang rings which show a pattern consisting of precipitate zones and clear spaces between them perpendicular to the diffusion direction. The provenance of the Fe^{+2}-rich solutions was possibly from the volcanic rocks, as it is indicated by the proximity of these structures to coeval volcanic rocks and by the existence of abundant iron minerals at the boundary between the sedimentary and volcanic rocks in outcrop.

The two different types of Liesegang rings studied here can be explained, according to Ortoleva (1994a), in relation to differences in sediment porosity. Liesegang rings consisting of different concentrations of iron hydroxides correspond to low-porosity sediments and very uniform grain-size. Liesegang rings composed of textural changes, observed in calcisiltite beds, can be accounted for by the generation from porous sediments in which fluid circulation gave rise to the progressive elimination of the matrix, and consequently to the selective concentrations of the peloids forming concentric rings, from a previous homogeneous distribution within the sediment.

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References

Büki, A., Kárpáti-Smidróczki, E. and Zrinyi, M. (1995a): *Jour. Chem. Phys.*, 103: 10387-10392.

Büki, A., Kárpáti-Smidróczki, E. and Zrinyi, M. (1995b): *Physica A*, 220: 357-375.

Bustillo, M.A. and Martín-Escorza, C. (1984): *I Congreso Español de Sedimentología*, 1: 159-171.

Carl, J.D. and Amstutz, G.C. (1958): *Bull. Geol. Soc. America*, 69: 1467-1468.

Chang, J.C. and Yortsos, Y.C. (1994): *Amer. Jour. Sci.*, 294: 137-172.

Chopard, B., Luthi, P. and Droz, M. (1994a): *Phys. Rev. Letters.*, 72: 1384-1387.

Chopard, B., Luthi, P. and Droz, M. (1994b): *Jour. Statistical Phys.*, 76: 661-677.

Cooper, R.F., Fanselow, J.B., Weber, J.K.R., Merkley, D. R. and Poker, D.B. (1996): *Science*, 274: 1173-1176.

Gindy, A.R., Al-Shakiry, A.J. and Sa'ad, N.A. (1985): *Jour. Sed. Petrol.*, 55: 762-768.

García-Hernández, M., López-Garrido, A.C., Rivas, P., Sanz de Galdeano, C. and Vera, J.A. (1980): *Geol. Mijnb.*, 59: 155-168.

García-Ruiz, J.M., Rondón, D., García-Romero, A. and Otálora, F. (1996): *Jour. Phys. Chem.*, 100: 8854-8860.

Heaney, P.J. and Davis, A.M. (1995): *Science*, 269: 1562-1565.

Henish, H.K. (1988): *Crystals in gels and Liesegang rings*. Cambridge Univ. Press, 198 p.

Henish, H.K. (1991): *Periodic precipitation*. Pergamon Press, 117 p.

Henish, H.K. and García-Ruiz, J.M. (1986a): *Jour. Cryst. Growth*, 75: 195-202.

Henish, H.K. and García-Ruiz, J.M. (1986b): *Jour. Cryst. Growth*, 75: 203-211.

Krug, H.J., Brandstadter, H. and Jacob, K.H. (1996): *Geol. Rundschau*, 85: 19-28.

Kuo, C.S., López-Cabarcos, E. and Bansil, R. (1997): *Physica A*, 239: 120-128.

Landmesser, M. (1988): *N. Jb. Mineral Abh.*, 159: 223-235.

Liesegang, R.E. (1913): *Geologische Diffusionen*. Steinkopff, 180 p.

López-Cabarcos, E., Kuo, C.S., Scala, A. and Bansil, R. (1996): *Phys. Review Letters*, 77: 2834-2837.

Moxon, T.J. (1996): *N. Jb. Mineral. M.*, 1: 21-36.

Molina, J.M., O'Dogherty, L., Sandoval, J. and Vera, J.A. (1999): *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 150: 309-330.

Ortoleva, P. (1994a): In *Diagenesis IV, Developments in Sedimentology*, 51: 79-94.

Ortoleva, P. (1994b): *Geochemical self-organization*. Oxford Univ. Press, 244 p.

Sanz de Galdeano, C. and Vera, J.A. (1992): *Basin Research*, 24: 21-36.

Shahabpour, J. (1998): *Geomorphology*, 22: 93-106.

Toramaru, A., Ishiwatari, A., Matsuzawa, M., Nakamura, N. and Arai, S. (1997): *Bull. Volcanol.*, 58: 393-400.

Vera, J.A. (1988): *Rev. Soc. Geol. España*, 1: 373-392.

Vera, J.A. and Molina, J.M. (1998): *Sedim. Geol.*, 119: 103-121.

Vera, J.A., Molina, J.M., Montero, P. and Bea, F. (1997): *Terra Nova*, 9: 163-166.