Radiometric dating and geochemistry of a tuff horizon from a mammal-bearing lacustrine sequence, Miocene Bicorp Basin, Eastern Spain.

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Abstract: The basin-fill sequence from the Bicorp Basin (Eastern Spain) comprises a lower alluvial unit and an upper lacustrine unit. The lower part of the lacustrine sequence includes a tuff bed, interbedded between two mammal-bearing horizons which have yielded fossil rodents characteristic of the MN 10 standard mammal unit (Late Vallesian, Late Miocene). K-Ar age determinations on the tuff have provided a radiometric age averaging 9.6 ± 0.2 Ma (weighted average of two samples) for this ash fall deposit. Major, trace and RE element analyses indicate that this tuff originated from a calc-alkaline event. The geochemical features of the Bicorp tuff, when compared with those from other calk-alkaline rocks from the Western Mediterranean, are not completely coincident. The stratigraphic correlation between the fossil mammal sites and the radiometrically-dated tuff allows a more precise calibration between the Late Miocene biochronological and geochronometric scales.

Key Words: K-Ar dating, Tuff, Lacustrine deposits, Miocene volcanism, Eastern Spain.

Resumen: El relleno sedimentario de la cuenca de Bicorp (Levante español) comprende una unidad inferior aluvial y una unidad superior lacustre. La parte inferior de la secuencia lacustre incluye un nivel de cenizas volcánicas intercalado entre dos niveles con mamíferos fósiles que han proporcionado restos de roedores característicos de la unidad standard MN 10 (Vallesiense superior, Mioceno superior). Las determinaciones de edad K-Ar en la cinerita han proporcionado una edad radiométrica promedio de 9,6±0,2 Ma para dicha cinerita. Los análisis de elementos mayores, traza y tierras raras indican que esta toba se originó a partir de un evento volcánico calco-alcalino. Las características geoquímicas de la cinerita de Bicorp son difíciles de encajar con las de otras rocas calco-alcalinas del Mediterráneo occidental. La correlación estratigráfica entre los niveles con mamíferos y la cinerita datada radiométricamente permite una calibración más precisa entre las escalas biocronológicas y geocronométricas para el Mioceno superior.

Palabras clave: Datación K-Ar, Cinerita, Depósitos lacustres, Volcanismo mioceno, Levante español.

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Volcanogenic horizons interbedded in sedimentary sequences provide valuable information on the volcanic events from which they originated and constitute suitable material for radiometric dating. These datings allow the biochronological scales to be calibrated with the geological events recorded in the basin fill sequences. However, the correlation between magnetostratigraphic, radiochronologic and biochronologic data are still scarce, and many of these correlations are controversial (see Snelling, 1985). Therefore, the sedimentary sequences that provide both biochronological and radiometric data bear a general interest for geochronology.

The Bicorp Basin, Eastern Spain, is one small Neogene non-marine basin which basin-fill sequence was claimed to have an age of Lower-Middle Miocene (Santisteban et al., 1989) on the basis of the finding of a fossil rodent tooth assigned to *Megacricetodon primitivus*. Another mammal site was found by one of us (N. L-M.) during exploration works linked to the project "Mapa Neotectónico y Sismotectónico de España" (Instituto Tecnológico Geominero de España). This mammal site yielded *Rotundomys* sp. and *Progonomys hispanicus*, indicating a Late Miocene age (Vallesian; López-Martínez, 1991, unpublished report). Recently, the finding of a thin tuff bed (less than 1 cm in thickness) in the Bicorp Basin, during fieldwork related to sedimentological and geochemical research by P.A., R.U. and A.V., encouraged us to search for mammal sites stratigraphically close to the tuff bed. As a result of this exploration a new mammal site has been reported (Anadón *et al.*, 1994; Anadón *et al.*, submitted).

The aims of this paper are to provide a K-Ar age for

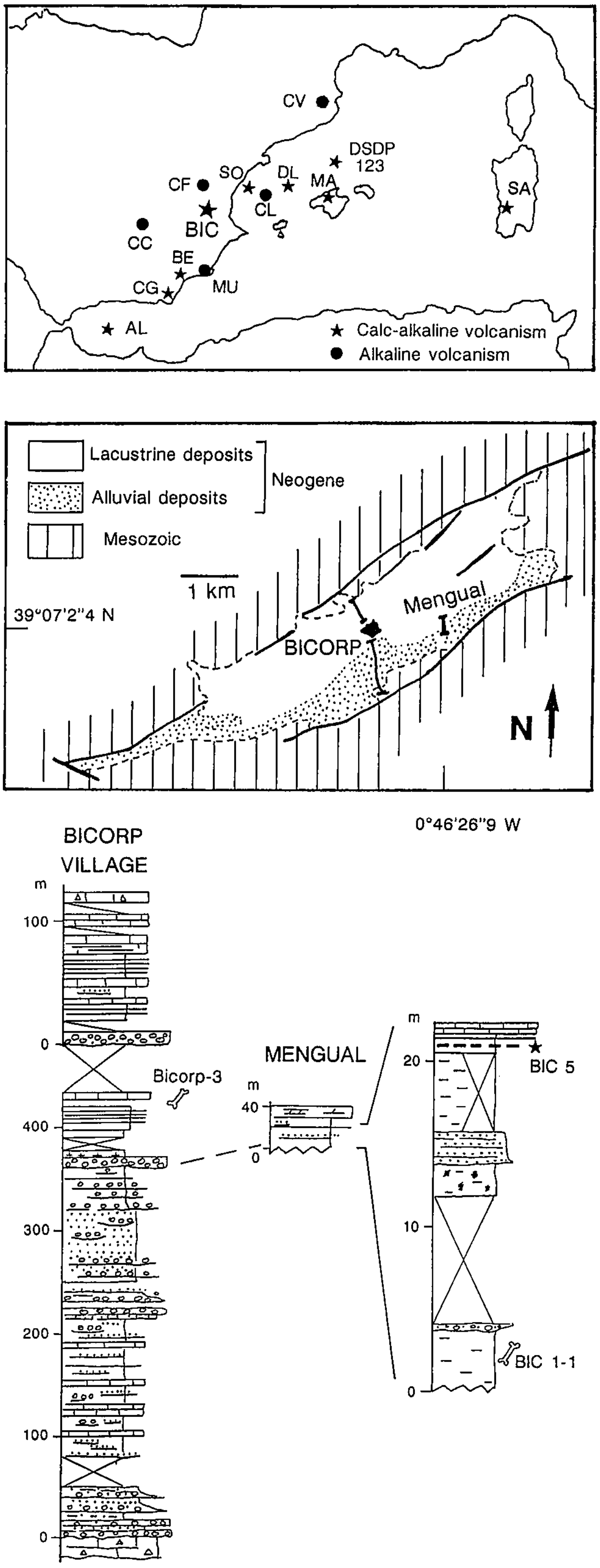

Figure 1.- A) Location of the Bicorp Basin (BIC) and distribution of Neogene magmatism in the Western Mediterranean. AL = Alborán Island, BE = Eastern Betics, CC = Campo de Calatrava, CF = Cofrents, CG = Cabo de Gata, CL = Columbretes Islands, DL = Delta J-1 oil well, DSDP - 123 = Deep Sea Drilling Project site 123, MA = Majorca (Puig de l'Ofre), MU = Murcia, SA = Sardinia, SO = Sagunto SO-1 oil well. B) Simplified map of the Bicorp Basin and location of the sections shown in C. C) Logs with the stratigraphic position of the mammal-bearing horizons and the tuff bed (*BIC 5).

the tuff, to describe the geochemical characteristics of the tuff and to place the ash fall episode in the framework of the Neogene volcanism of the Western Mediterranean in which the data on the geochemical features and dating of volcanic episodes are still scarce (cf. Martí *et al.*, 1992).

Geological setting. Stratigraphy of the Bicorp Basin.

The Miocene Bicorp Basin (Eastern Spain) is a small (14 km^2) ENE-WSW-elongated basin which is located between the Eastern Iberian Range and the Prebetics (northern domain of the Betic Chain). The origin of the Bicorp Basin was linked to a Middle to Late Neogene extensional phase in which both normal faulting affecting a Jurassic-Cretaceous sequence and the diapirism of Triassic mudstones and evaporites gave rise to small basins in Eastern Spain (Moissenet 1985; Anadón *et al.*, 1989; Roca, 1992; Roca and Guimerà 1992).

The Miocene basin fill comprises a sequence over 650 m thick formed by a lower alluvial-dominated unit, about 400 m thick, and an overlying lacustrine-dominated unit (Santisteban *et al.*, 1989; Anadón *et al.*, 1994).

Santisteban *et al.* (1989) report mammal fossil remains ascribed to *Megacricetodon primitivus* from a site which may be placed in the transitional facies of the lower part of the lacustrine unit, but without a more precise location. Other mammal sites with no precise location, ranging from the Upper Aragonian to the Upper Vallesian have been listed by Santisteban *et al.* (1994).

The tuff that we report is situated in the transitional facies of the lower part of the lacustrine unit in the Mengual section (Fig. 1). In this section, the lower transitional lacustrine facies include one thin tuff bed (BIC-5), 7-8 mm thick, which is intercalated between a grey laminated mudstone interval, 0.8 m in thickness. These laminated mudstones overlie a sequence up to 20 m thick formed of massive, grey and brown sandy mudstones with interbedded sandstones. The outcrop was cleaned by means of an excavation 5 m in strike, in order to obtain fresh samples, without recent alteration products. In the tuff-bearing sequence several beds contain mammal remains, but only the lower mammal-bearing horizon (BIC 1-1), about 19 m below the tuff bed, has provided us with a significant micromammal fauna which may be attributed to the Late Vallesian (Anadón et al., submitted).

Methods.

K-Ar dating

Preliminary X-ray fluorescence spectroscopy (XRF) analyses performed on whole rock samples of the tuff bed yielded a K_2O content of 2.8 %. K-Ar analyses were performed in the following way: 100 g of cleaned tuff fragments were used for both whole rock analysis and for separation of 1-2 g of mineral concentrate. The fraction to be dated was crushed, sieved to less than 77 µm and homogenized. It was treated with very dilute HF and HNO_3 to remove carbonates, secondary clay minerals, devitrified glass and zeolites. Any remaining zeolite (material density < 2.55) was removed using heavy liquids and a concentration of primary K-feldspar fraction was obtained.

The argon extractions were performed by induction heating fusion in a specially designed ultra-high vacuum system. The extraction line was directly coupled to a MS-10 mass spectrometer (Associated Electrical Industries). The standard USGS LP-6 (Biotite) was used. All argon extractions were performed in duplicate to ensure accuracy of the analyses. Potassium analyses were performed in triplicate, using separate aliquots of the sample. A flame spectrophotometer was used for potassium analyses. The overall analytical error for the studied samples is less than 3%, although it decreases to 1.7% for the weighted average.

The decay constants and the K abundance used for age calculations were those recommended by Steiger and Jäger (1977).

Chemical analyses.

In order to evaluate the geochemical features of the volcanism linked to the tuff bed, two cleaned tuff samples (D-2 and D-3) were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) after fusion for whole rock analysis, ICP-MS after total digestion for trace metals (Cu, Pb, Zn, Ag, Ni, Cd, Bi, V and Be) and Instrumental Neutron Activation Analysis (INAA) for trace elements, including rare earth elements (REE). In addition, X-ray Fluorescence Spectroscopy (XRF) on pressed pellets was used for elements such as Pb, Ga, Sn, S, Nb and Rb.

Composition and K-Ar dating of the tuff.

Mineralogy and petrology.

The tuff bed (BIC 5) is 7 to 8 mm thick. It is interbedded within dark grey laminated mudstones. The mudstones contain abundant vegetal debris (seeds, coalified wood fragments). In thin section the tuff consists of a cryptocrystalline brownish matrix that encloses sanidine phenocrysts and few scattered small zeolite crystals. The amount of sanidine crystals, after microscopic estimation is about 15% of the rock. The main population of these crystals has a grain size between 30 μm and 100 μm. The sanidine crystals are mainly subhedral, but almost all of them appear broken. In this case they show straight or convex faces or, in some of them, one face appear serrate. Sanidine crystals with very sharp points are common. Very few crystals show corroded resorption borders. The extintion for the sanidines vary from normal to oscillating or patching extinction. Some less disturbed crystals display carlsbad twins. Rare, small-sized plagioclase blades are also present. Minor chlorite anhedral crystals are also present as secondary products, probably derived from biotite crystals. Most of the matrix is derived from the original glass which has been devitrified to fine grained early alteration products.

The scanning electron microscope (SEM) observations indicate that the tuff is formed by a fine grained matrix (< 2 μm) with a few euhedral and subhedral larger zeolite crystals (20-100 μm) and heterogranular K-feldspar crystals (Fig. 2). X-ray diffraction (XRD) analyses indicate that the tuff is mainly composed of Na sanidine and a zeolite of the heulandite-clinoptilolite group. The energy dispersive X-ray (EDX) analyses on the sanidine crystals shows the predominance of K and the presence of noticeable amounts of Na (sanidine-anorthoclase). Similar observations on zeolite crystals show the presence of Ca and K and minor amounts of Mg in some of them. This cation composition also suggests a heulandite adscription.

The textural features of the tuff, particularly the grain size, indicate that this is a distal ash fall deposit with a high degree of fragmentation. This suggests that the eruption mechanism that generated the tuff was a plinian to ultraplinian magmatic eruption or any kind of phreatomagmatic eruption (Cas and Wright, 1988).

The alteration of ash fall deposits in lacustrine (mainly saline) environments has been widely documented. The resulting products depend on the composition of the ash and the chemistry of the lake waters. A typical

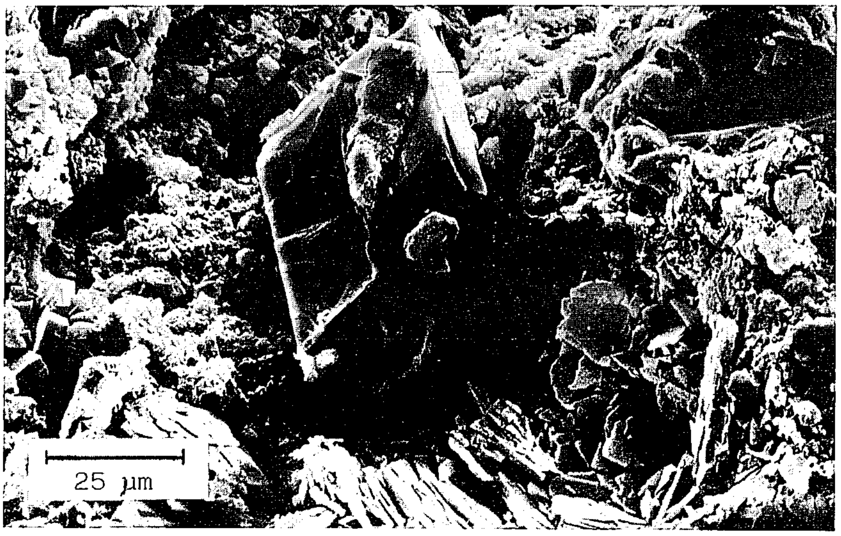

Figure 2.- SEM micrograph of the Bicorp tuff (BIC-5). Sanidine crystal in a fine grained matrix of sanidine and zeolite.

alteration sequence might be glass altering to a zeolite, such as clinoptilolite, which may alter to analcime, which in turn may be replaced by authigenic K-feldspar (Hay, 1966, 1983; Sheppard and Gude, 1968; Eugster and Hardie, 1978; Kastner and Siever, 1979; Surdam, 1983). In some cases, zeolites are isochemical with the volcanic glass and can form simply by the addition of water (e.g. trachyte glass; Surdam and Eugster, 1976). In this case, although an alteration process after glass formation may be invoked for the genesis of the zeolites, the sanidine features indicates that a primary volcanic origin must be defined for the K-feldspar. The authigenic, low temperature K-feldspars in sedimentary rocks, which in some cases have been reported as sanidines on the basis of XRD and chemical composition, are characterized by the high chemical purity, almost the extreme K end member of the alkali feldspar series (Kastner and Siever, 1979). Woodard (1972) describes an authigenic sanidine with Na_2O/K_2O ratio of 0.0026. The volcanogenic sanidines may have a variable Na_2O/K_2O ratio, usually from 0.2 to 0.9 (eg. Deer *et al.*, 1971; p. 301). In the case of the sanidines from the Bicorp tuff, the spacing of the 201 planes after XRD, as well as the EDX measurements (see above) reveal a noticeable content of Na for this alkali feldspar. These data indicate a volcanic origin for these sanidines.

The crystal morphology of the Bicorp sanidines provides also additional indicators for their origin. The authigenic low temperature K-feldspars in sedimentary rocks display subhedral to euhedral forms (Marshall *et al.*, 1986), although anhedral forms have also been reported (Kastner and Siever, 1979). The sanidines from the Bicorp tuff are subhedral, although in many cases exhibit triangular or trapezoidal shapes with broken surfaces. Crystal fragmentation is a typical feature of pyroclastic material derived from explosive eruptions. Concluding, the sanidine from the Bicorp tuff has a volcanogenic origin and therefore the dating has been performed on a primary, syngenetic mineral of the ash fall deposit.

Geochemistry

Two samples of the tuff (D-2 and D-3) were selected for geochemical analyses. The results obtained are shown in Table I. Since loss of ignition (LOI) values were high (14,8-16,8% respectively) we have recalculated the major element content to a 100% water free basis. In this case the large amount of LOI is due to the high content in crystallisation water of the zeolites, and therefore it not corresponds to a recent alteration of the tuff. These samples show a dacite-rhyolite composition when using the total alkalis/silica (TAS) diagram (Fig. 3). The composition is confirmed as dacitic if REE chondrite normalized diagram is used (Fig. 4). Figure 3 also shows the fields of other calc-alkaline volcanic rocks from the surrounding Western Mediterranean areas. There is no overlap between the Bicorp samples and the other volcanic rocks from the Western Mediterranean. We have only used major element diagrams for comparative purposes because the

Table I.- Major, trace and RE element concentrations of the Samples Studied With indication of the used analytical methods.

Sample	**D-2**	**D-3**	Detec. limits
Fusion ICP (recalculated 100 % water free)			
SiO_2	71.18	74.44	0.01%
TiO_2	0.42	0.32	0.01%
Al_2O_3	18.24	16.1	0.01%
Fe_2O_3	2.25	1.98	0.01%
MnO	0.02	0.02	0.01%
MgO	1.39	0.98	0.01%
CaO	1.27	1.08	0.01%
Na_2O	2.05	1.90	0.01%
K_2O	3.14	3.14	0.01%
P_2O_5	0.04	0.04	0.01%
TOTAL	100.00	100.00	
Fusion ICP (in ppm)			
Ba	106	137	1ppm
Sr	1997	2085	1ppm
Y	9	7	1ppm
Zr	170	172	1ppm
XRF pressed pellet (in ppm except S)			
Pb	<5	7	5ppm
Ga	25	35	5ppm
Sn	7	8	5ppm
S (%)	0.26	0.28	50ppm
Nb	47	51	2ppm
Rb	56	59	2ppm
Total digestion ICP (in ppm)			
Cu	3	3	1ppm
Zn	46	46	1ppm
Ni	2	2	1ppm
V	7	6	1ppm
INAA (in ppm, except Au)			
Au (ppb)	<2	2	1ppb
As	3	3	1ppm
Br	1.4	1.3	0.5ppm
Co	1.8	1.7	0.1ppm
Cr	1.9	1.2	0.5ppm
Cs	<0.2	0.6	0.2ppm
Hf	6.4	5.4	0.2ppm
Mo	4	2	2ppm
Sb	1	1	0.1ppm
Sc	1.8	1.5	0.01ppm
Se	2.7	2.3	0.5ppm
Ta	5.7	5.5	0.3ppm
Th	6.7	8.2	0.1ppm
U	2.2	2.9	0.1ppm
La	35.2	38.2	0.5ppm
Ce	65	76	1ppm
Nd	22	29	1ppm
Sm	3.95	4.35	0.01ppm
Eu	0.79	0.93	0.05ppm
Tb	0.5	0.7	0.1ppm
Yb	1.32	1.54	0.05ppm
Lu	0.17	0.18	0.01ppm

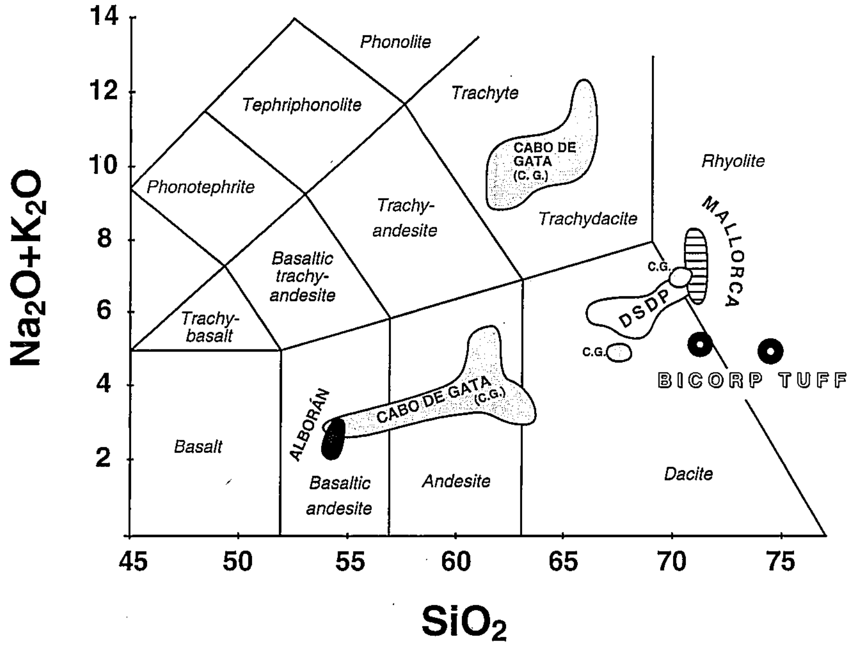

Figure 3.- Total alkalis/silica (TAS) diagram. The Bicorp tuff, shown as black and white dots, falls on the dacitic and rhyolitic fields close to the fields of the DSDP (123 site) and Mallorca volcanics. Other Western Mediterranean volcanic areas are represented.

analyses of the Western Mediterranean volcanics reported in the references are not complete.

The concentration of some major, trace and RE elements normalized to primitive mantle have been plotted (Fig. 5) using the diagram proposed by Hofmann (1988). The Bicorp tuff samples are slightly enriched in Rb, U, Th, LREE, K, Hf, Zr, very enriched in Nb, Sn, and exhibit anomalously high enrichment in Sr. They are slightly depleted in Ba, Na, Y, Ti, and HREE and highly depleted in the more compatible elements (Cu to Ni) with respect to the average continental crust (Fig. 5). The Rb and Hf contents, the slight enrichment in LREE and in the more compatible elements indicate a normal dacitic-rhyolitic pattern. However, the high content of Sr cannot be explained in such a way. Sr is known for its effectiveness in substituting for Ca in plagioclases, but the presence of this mineral in our samples is not important. Thus, Sr which is present in relatively high amounts in lacustrine environments, could have been added during diagenesis. In fact, diagenetic celestite is present in a large number of beds of the Bicorp lacustrine sequence.

K-Ar dating

Two K-feldspar concentrate samples (D-0 and D-2) were selected for K-Ar dating. The results are shown in Table II. The ages obtained on K-feldspars are 9.7 ± 0.3 and 9.5 ± 0.3 Ma. The K-Ar ages from two samples of the concentrate of feldspar phenocrysts (anorthoclase-sanidine) are slightly older than a previous age derived from one whole rock sample (8.9 ± 0.3 Ma). This means that the glass has lost Ar during alteration processes. Thus, feldspar ages are more reliable than the whole rock

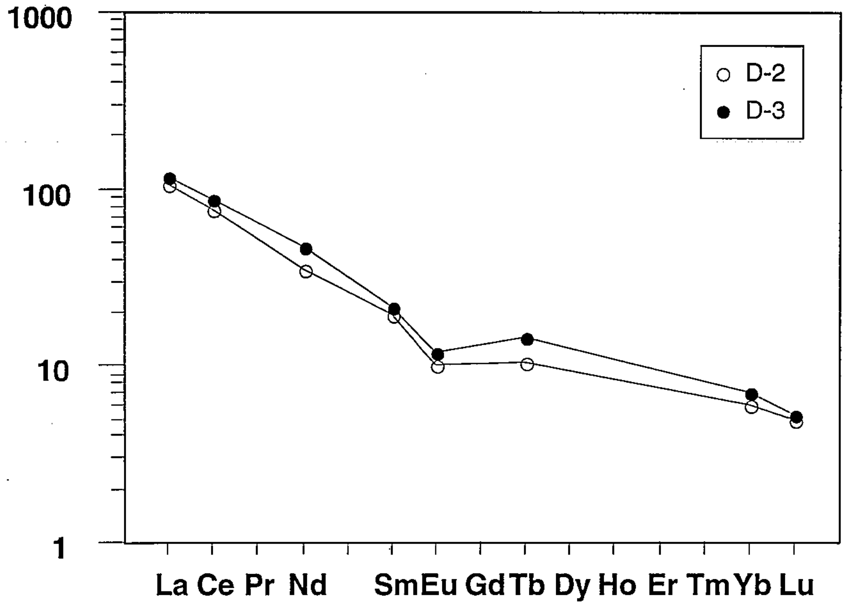

Figure 4.- REE spider diagram normalized to chondrite (after Nakamura, 1974) for the Bicorp tuff samples. Yaxis is the ratio rock/chondrite. A very common dacite trend is deduced.

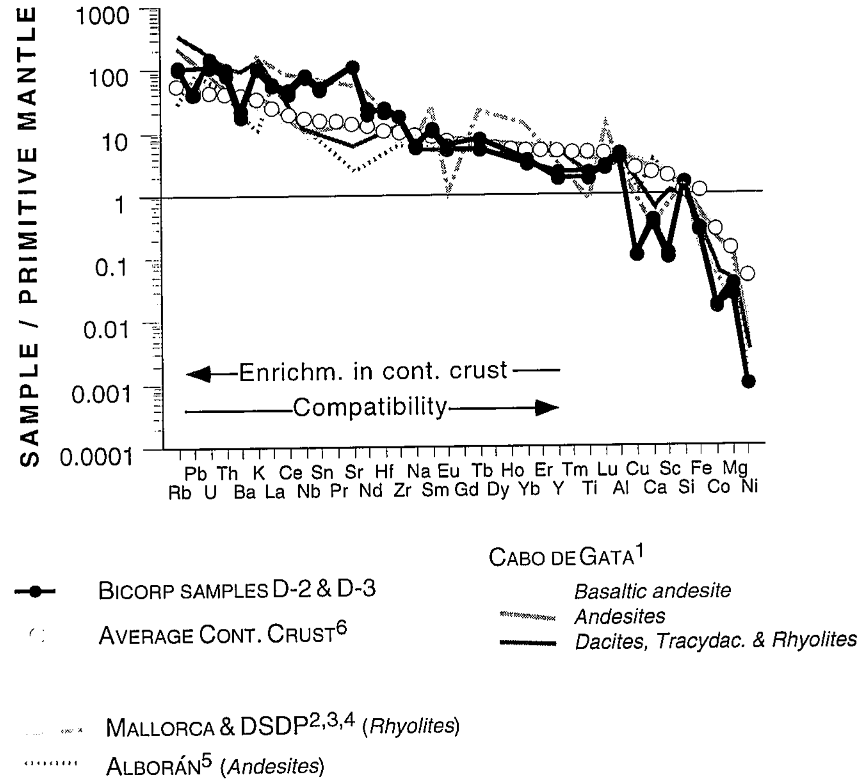

Figure 5.- Normalization diagram to primitive mantle after Hofmann (1988). References: 1= Di Batistini et al. (1987); 2,3,4 = Riviére et al. (1981), Mitjavila et al. (1990), Martí et al. (1992); 5 = Aparicio et al. (1991); 6 = Taylor and MacLennan (1985). As a reference line (6) we have plotted the continental crust average after Taylor and McLennan (1985). The line for each represented zone is the average value from all the analyses for each zone. Only for the Cabo de Gata values, we have represented 3 averages depending on the chemistry of the samples. The data for some elements are not avalaible for all the zones (e.g. Mallorca anlyses only comprise major and RE elements). In these cases the values for missing elements have been extrapolated.

dating. From both measurements on concentrates, sample D-2 gives the best results. It has the highest K content and the best $^{40}Ar^{*}/^{40}Ar_{T}$ ratio. Nevertheless, the results for both K-feldspar concentrates are statistically indistinguishable and the weighted average age for the Bicorp tuff is 9.6 ± 0.2 Ma with a 95% confidence limit and a statistically satisfactory dispersion (MSWD= 0.889).

Relationship between the Bicorp tuff and the Neogene volcanism in the Western Mediterranean

The averaged 9.6 ± 0.2 Ma apparent age calculated for the volcanic episode which generated the Bicorp tuff corresponds to the Upper Miocene (Lower Tortonian equivalent to the Upper Vallesian). A comparison among all known ages of the Miocene to Quaternary volcanism in the Western Mediterranean may be found in Martí *et al.* (1992).

Table II.- K-Ar age determinations on Bicorp tuff samples.

Sample	Description	% K	$^{40}Ar^{*}$ (ppm)	$^{40}Ar^{*}/^{40}Ar_{t}$	Age (Ma)±2σ
D-0	K-feldspar	4.987	0.003362	0.310	9.7±0.3
		4.825	0.003257	0.470	
D-2	K-feldspar	5.200	0.003434	0.561	9.5±0.3
		5.407			
		5.309	0.003545	0.655	

The dacites and rhyolites of DSDP site 123 and Puig de l'Ofre (Majorca) respectively, despite being some of the geographically and geochemically closer calc-alkaline volcanic rocks, give ages between 24.4 to 18.6 Ma. (Ryan *et al.*, 1972; Rivière *et al.*, 1981; Mitjavila *et al.*, 1990). These ages are too old to be compared with our results. Also the calc-alkaline volcanism in Sardinia, being aged between 32.3 to 11.6 Ma, is too old to be correlated with our results. The two youngest ages from this volcanic area are 11.6 and 11.9 Ma and they correspond to the same ignimbrite, all the other Sardinian ages being older than 15.1 Ma (Beccaluva *et al.*, 1985).

The volcanic Alborán Island (Western Mediterranean) is formed by a succession of andesitic pyroclastic deposits. The ages of two fragments of the pyroclastic deposits are 18.18 and 7.49 Ma respectively (Aparicio *et al.*, 1991). The geochemistry and age range of these rocks do not allow any correlation with the Bicorp tuff.

In the Valencia trough, several exploration oil wells contain volcanic sequences that range from few meters to up to 100 m thickness. K-Ar ages were obtained from volcanic rocks from two wells (8.0 and 11 to 15 Ma; in Roca, 1992). However, the radiometric age of these rocks does not correlate with the stratigraphy of the drills, and therefore the ages of these volcanic rocks must be regarded with caution (Roca, 1992). The detailed geochemistry of these rocks is, however, not reported, with only the general description as calc-alkaline rocks provided.

The pyroxene andesites, high K-dacites and amphibole-rich andesites, dacites and rhyolites of Cabo de Gata (SE Spain) give ages ranging between 12 to 7.5 Ma (Di Battistini *et al.*, 1987). The amphibole-rich rocks are slightly older than our samples (from 12.4 to 11.6 Ma) but the youngest is close to our result. This young sample was dated using groundmass instead of mineral separates, and therefore this is not reliable data. The high-K dacites give ages between 11.6 Ma (on biotite) to 10.8 Ma (groundmass) with one sample being 6.9 Ma (biotite). The pyroxene andesites have ages between 12.0 to 7.5 Ma. Some of these pyroxene andesites have ages around 8.6 and 10.8 Ma, very close to the apparent age of the Bicorp tuff.

The Bicorp tuff is coincident in time, but neither in composition nor in geodynamical setting, with the first manifestations of alkaline volcanism in the Iberian peninsula. In the Catalan volcanic province, alkaline volcanism started 10 Ma. ago with eruption of trachytes and basanites that lasted until present, with the eruption of basalts (see summary in Martí *et al.*, 1992). In the Campos de Calatrava zone (Central-south Spain) alkaline volcanism started at 7.7 Ma (with one sample dated 17.5-14.2 Ma) and ended 1.75 Ma ago (Ancochea *et al.*, 1979). Other areas with alkaline volcanism (Columbretes, Cofrentes, and Cartagena and Murcia) show ages between 7 Ma to present (Aparicio *et al.*, 1991; Saez-Ridruejo and López Mariñas, 1975; Bellon *et al.*, 1983, respectively).

The geochemistry of the Bicorp tuff when compared with the other calc-alkaline rocks of the area, even with those closer in age, is not coincident with any of them. This fact could indicate that the Bicorp ash fall deposit may be related to a far eruption since ashes can travel thousands of kms. If the Bicorp tuff was related to a volcanic eruption from the Western Mediterranean area it is likely that it was one of the last events of the calc-alkaline cycle in the Western Mediterranean (See Martí *et al.*, 1992, for a complete summary of the calc-alkaline and alkaline cycles in the Western Mediterranean volcanism).

Conclusions

The basin fill sequence from Bicorp comprises a lower alluvial unit and an upper lacustrine unit. The lowermost part of the lacustrine succession in the center of the basin includes a thin tuff bed which is located 19 m stratigraphically over a mammal-bearing horizon which has provided an Upper Vallesian age. The tuff is composed of diagenetic zeolites, as an alteration product of the original volcanic glass, and volcanogenic sanidines. K-Ar age determinations on the sanidine crystals from the tuff have provided a radiometric age averaging 9.6 ± 0.2 Ma for the ash deposit. The geochemistry of the Bicorp tuff indicates that it was linked to a dacitic-rhyolitic volcanic event. An important difference with normal dacitic-rhyolitic composition is the high Sr content. Strontium may be abundant in lacustrine environments and may have been added during diagenesis. The geochemical features of the Bicorp tuff, when compared with other volcanic rocks from the Western Mediterranean, do not show full coincidence with any of them. This would indicate that the ash came from an unlocated volcano far from the Western Mediterranean Area.

The Bicorp mammalian associations (Bicorp-3 and BIC 1-1) together with the radiometric age indicate that the final configuration of the basin is coeval or posterior to the Upper Vallesian. The stratigraphic correlation between the fossil mammal sites and the radiometrically-dated tuff allows to make the calibration of the Upper Miocene biochronological and geochronometric scales more precise. The Bicorp tie point contributes to this calibration for a time span which has scarce anchor points for correlation. It constrains the calibration of the Late Vallesian (MN 10 unit) to around 9.7 Ma.

SEM observations and EDX analyses were carried out at the Servei de Microscòpia Electrònica (Serveis Generals, Universitat de Barcelona, Spain). XRD and some preliminary XRF analyses were performed at the Institut de Ciències de la Terra "J. Almera". Trace element and whole rock analyses were performed at the Activation Laboratories (Ontario, Canada). K-Ar dating was made at the Krueger Laboratories, Cambridge, Massachussets (USA). Thaks to Dr. F. Plana and Dr. I. Queralt for their ad vise in the SEM and XRD identification of the zeolites. This work has been partially supported by CICYT Project PB 90-0080. Thanks to Dr. I. Zamarreño and Dr. E. Roca for their helpful comments on a draft of the paper. Dr N. Pearce is gratefully acknowledged for comments on a previous version of the manuscript. The referees of the Revista de la Sociedad Geológica de España are also gratefuly acknowledged for the helpful revision of the manuscript. Some of their comments and observations have been incorporated in the paper.

References

Anadón, P., Cabrera, L., Julià, R., Roca, E. and Rosell, L. (1989): Lacustrine oil-shale basins in Tertiary grabens from NE Spain (Western European rift system). *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 70: 7-28.

Anadón, P., Robles, F., Roca, E., Utrilla, R. and Vázquez, A. (1994): Evolución tectonosedimentaria de la cuenca miocena de Bicorp (Macizo de Carroig, Valencia). *Comunicaciones del II Congreso del G.E.T. Simposio (IGCP nº 324)*: 227-229.

Anadón, P. López-Martínez. N., Mitjavila, J. M., Utrilla, R. and Vazquez, A. (submitted, *Geobios*). New Late Miocene mammal sites correlated with the radiometric scale from the Bicorp Basin (Eastern Spain).

Ancochea, E., Giuliani, O. and Villa, I. M. (1979): Edades radiométricas K-Ar de la región central española. *Estudios Geológicos*, 35: 131-135.

Aparicio, A., Mitjavila, J. M., Araña. V. and Villa, I. M. (1991): La edad del volcanismo de las islas Columbrete Grande y Alborán (Mediterráneo occidental). *Bol. Geol. Min.*, 102: 562-570

Beccaluva, L., Civetta, L., Macciotta, G. and Ricci, C. A. (1985): Geochronology in Sardinia: results and problems. *Rend. Soc. Ital. Mineral. Petrol.*, 40: 57-72

Bellon, H., Bordet, P. and Montenat, C. (1983): Chronologie du magmatisme Néogène des Cordillères Bètiques (Espagne Meridionale). *Bull. Soc. Géol. Fr.*, 25: 205-217.

Cas, R. A. F. and Wright, J. V. (1988): *Volcanic successions. Modern and ancient.* Unwin Hyman, London, 528 p.

Deer, W.A., Howie, R.A. and Zussman, J. (1971). *An introduction to the rock-forming minerals.* Longman. London. 527 p.

Di Battistini, G., Toscani, L., Iaccarino, S. and Villa, I. M. (1987): K/Ar ages and the geological setting of calc-alkaline volcanic rocks from Sierra de Gata, SE Spain. *N. J. Min. Monat.*, 8: 369-383.

Eugster, H. P. and Hardie, L. A. (1978): Saline Lakes. In: *Lakes. Chemistry, Geology, Physics* (Lerman, A., ed.). Springer. New York, p 237-293.

Hay, R. L. (1966): Zeolites and zeolitic reactions in sedimentary rocks. *Geol. Soc. Am. Sp. Paper*, 85: 1-130.

Hay, R. L. (1983): Geology of zeolites in sedimentary rocks. In: *Mineralogy and Geology of natural zeolites* (Mumpton, F.A. ed.) *Rev. Min.*, 4: 53-64.

Hofmann, A. W. (1988): Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth Planet. Sci. Lett.*, 90: 297-314.

Kastner, M. and Siever, R. (1979): Low temperature feldspars in sedimentary rocks. *Amer. Jour. Science.*, 279: 435-479.

López-Martínez, N. (1991): *Informe sobre los yacimientos de micromamíferos de Levante.* Mapa Neotectónico y Sismotectónico de España. Informe Complementario (Dataciones Relativas). *Inst. Tec. Geomin. España. Unpublished report.*

Marshall, B.D., Woodard, H.H.,and De Paolo, D.J. (1986): K-Ca-Ar systematics of authigenic sanidine from Wakau, Wisconsin, and the diffusivity of argon. *Geology*, 14: 936-938.

Martí, J., Mitjavila, J. M., Roca, E., Aparicio, A. (1992): Cenozoic magmatism of the Valencia Trough (Western Mediterranean): Relationship between structural evolution and volcanism. *Tectonophysics*, 203: 145-165.

Mitjavila, J. M., Ramos-Guerrero, E. and Martí, J. (1990): Les roches pyroclastiques du Puig de l'Ofre (Serra de Tramuntana, Majorque): Position géologique et datation K-Ar. *C. R. Acad. Sci. Paris*, 31 (Série II): 687-692.

Moissenet, E. (1985): Les dépressions tarditectoniques des Chaines Ibériques méridionales: distension, diapirisme et dépôts néogènes associés. *C. R. Acad. Sci. Paris*, 30 (Série II): 523-528.

Nakamura, N. (1974): Determination of REE, Ba, Fe, Mg, Na, and K in carbonaceous and ordinary chondrites. *Geochim. Cosmochim. Acta*, 38: 757-775.

Riviére, M., Bellon, H. and Bonnot-Courtois, C. (1981): Aspects géochimiques et géochronologiques du vulcanisme pyroclastique dans le Golfe de Valence: site 123 DSDP, Leg 13 (Espagne)- Consequences géodynamiques. *Mar. Geol.*, 41: 295-307.

Roca, E. (1992): *L' Estructura de la conca Catalano-Balear: Paper de la Compressió i de la Distensió en la seva gènesi.* Ph.D. Thesis, University of Barcelona, Unpublished, 330 p.

Roca, E. and Guimerà, J. (1992): The Neogene structure of the eastern Iberian margin: structural constraints on the crustal evolution of the Valencia trough (western Mediterranean). *Tectonophysics*, 203: 203-218.

Ryan, W. B. F., Hsü, K. J., Honnorez, J., Weibel, M., Cann, J. R., Ferrara G., Bigazzi, G., Bonadonna, F. P. and Giuliani, O. (1972): Petrology and geochemistry of the Valencia Trough volcanic rocks. *Init. Rep. DSDP.*, 13: 767-773.

Sáez-Ridruejo, C. and López Mariñas, J. M. (1975): La edad del volcanismo de Cofrentes (València). *Tecniterrae*, 6: 8-14.

Santisteban, C. de, Ruíz-Sánchez, F. J. and Bello, D. (1989): Los depósitos lacustres del Terciario de Bicorp (Valencia). In: *Sistemas Lacustres Cenozoicos de España.* (Anadón, P. and Cabrera, L., eds.) *Acta Geol. Hisp.*, 24: 299-307.

Santisteban, C. de, Ruíz-Sánchez, F. J. and Lacomba, J. I. (1994): Estratigrafía, edad y evolución de los depósitos terciarios de la cuenca de antepaís de Quesa-Bicorp (Valencia). *II Congreso del G.E.T., Comunicaciones*: 209-212.

Sheppard, R. A. and Gude, A. J. (1968): Distribution and genesis of athigenic silicate minerals in tuffs of Pleistocene Lake Tecopa, Inyo County, California. *U. S. Geol. Surv. Prof. Paper.*, 63: 1-38.

Snelling, N. J. (ed.) (1985): The Chronology of the Geological Record. *Mem. Geol. Soc. London*, 10: 1-343.

Steiger, R. H. and Jäger, E. (1977): Subcommission on Geochronology: Convention on the use of decay constants in Geo- and Cosmochronology. *Earth Planet. Sci. Lett.*, 36: 359-362.

Surdam, R. C. (1983): Zeolites in closed hydrologic systems. In: *Mineralogy and Geology of natural zeolites* (F.A. Mumpton, ed.). *Rev. Mineral.*, 4: 65-91

Surdam, R. C. and Eugster, H. P. (1976): Mineral reactions in the sedimentary deposits of the Lake Magadi Region, Kenya. *Bull. Geol. Soc. Am.*, 87: 1739-1752.

Taylor, S. R. and McLennan, S. M. (1985): *The continental crust: Its composition and evolution.* Blackwell. Sci. Publ., 312 p.

Woodard, H. H. (1972) Syngenetic sanidine beds from Middle Ordovician Saint Peter Sandstone, Wisconsin. *Jour. Geology*, 80: 323-332.

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