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USE OF QUATERNARY TRAVERTINES OF CENTRAL-SOUTHERN ITALY AS ARCHIVES OF PALEOCLIMATE, PALEOHYDROLOGY AND NEOTECTONICS

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ABSTRACT: A. Bertini et al., *Use of Quaternary travertines of central-southern Italy as archives of paleoclimate, paleohydrology and neotectonics.* (IT ISSN 0394-3356, 2008).
This paper reports how travertine of central-southern Italy, formed in response to the extensive circulation of waters inside the regional aquifer hosted in the Mesozoic carbonate sequences, can be used as a tool for paleoclimatic, neotectonic and paleohydrological investigations.
CO_2-rich thermal springs, CO_2 vents and travertine are frequent occurrences of the peri-Tyrrhenian sector of central-southern Italy. In a crust affected by mantle magmas triggering fluids motion, among others CO_2 from several horizons at variable depth, the $\delta^{13}C$ of CO_3-ions of dissolved travertine suggests the type of circulation and the prevalent CO_2 source involved. More negative values suggest "normal" topographically driven circulation in karstic circuits, where CO_2 derives from soil (bacteria); more positive values suggest the inflow into the karstic circuits of deep CO_2. Such rising CO_2, together with other acidic gases (e.g. H_2S) greatly enhances limestone dissolution. Accordingly, the travertine formed at the surface (metheogene vs thermogene) reflects the type of "mother" CO_2 involved in the dissolution process. In this way, travertine can be used to trace the evolution of paleohydrothermal systems in areas where there are no thermal features at surface.
In terms of tectonic tool, since active and fossil travertine in the Apennines can be found at very different elevations, their formation age reflects the difference in elevation between the present and the past karstic circulation. Being the Apennines a young, very active orogen, the described methodology of using travertine as a benchmark for paleohydrology, suggests for a vertical isostatic rate of 0.7 mm/y.
Being very sensitive to environmental conditions, travertine can also be used as a tracer for paleoclimate. The parallel investigation on the stable isotopic composition ($\delta^{18}O$, $\delta^{13}C$) of the dissolved CO_3-ions, and palynological profiles in two Pleistocene deposits of central Italy (Serre di Rapolano and Tivoli, the latter in progress), allowed to describe variations in the last ca 120 kyrs. The correspondence between observed environmental fluctuations in pollen and isotopes, as well as with other proxies in nearby terrestrial deposits, and with more global proxies (ice-core and foraminifera) seems possible and demonstrates that travertine can be used to investigate the paleoclimate of the late Quaternary. This is in line with the observation that most of dated travertine in central Italy cluster in interglacial periods. This coincidence seems reasonable: 1) because the deposition of travertine is depending upon rainfall amounts, and 2) because in glacial periods, the lower level of the oceans also lowers the base level of karstic circulation.

RIASSUNTO: A. Bertini et al., I travertini quaternari dell'Italia centro-meridionale come archivio per studi paleoclimatici, paleoidrologici e sulla tettonica attiva*. (IT ISSN 0394-3356, 2008).*
La diffusa presenza nel settore peri-tirrenico dell'Italia centro-meridionale di sorgenti termali, emissioni gassose a CO_2, nonché di numerosi depositi di travertino (fossili ed attuali) formatisi in seguito alla circolazione carsica in acquiferi regionali confinati nelle sequenze carbonatico-mesozoiche, offre la possibilità di indagare il possibile utilizzo dei travertini stessi per ricostruzioni paleoambientali, paleoclimatiche, paleoidrologiche e neotettoniche.
In una crosta in cui magmi del mantello favoriscono la formazione secondaria di CO_2 metamorfica a vari livelli di profondità, che risalendo entra nell'acquifero carbonatico regionale, esiste uno stretto legame tra la composizione isotopica del carbonato dei travertini e la composizione isotopica della CO_2 disciolta nell'acqua da cui i travertini stessi precipitano. Conseguentemente, il $\delta^{13}C$ dei travertini suggerisce il tipo di circolazione e la sorgente prevalente della CO_2 che li ha generati. In particolare, valori negativi suggeriscono una circolazione di tipo carsico, superficiale, con CO_2 derivata dall'alterazione del materiale organico del suolo; valori più positivi, indicano invece la prevalenza di CO_2 più profonda, che, risalendo insieme ad altri gas acidi, eventualmente presenti (e.g. H_2S), aumenta la dissoluzione dei carbonati. I depositi di travertino che si formano in superficie, riflettono il tipo di CO_2 "madre" che è coinvolta nei processi di dissoluzione (meteogenici o termogenici). I travertini possono quindi essere utilizzati per mettere in luce la presenza di antichi sistemi idrotermali anche laddove non si hanno più evidenze superficiali di questo tipo. In Italia, muovendosi dal settore occidentale peri-tirrenico verso quello orientale adriatico, si osserva una chiara relazione spaziale tra differenti tipi di travertino. Depositi termogenici (travertini s.s.*), associati a sorgenti termali, sono diffusi nel versante tirrenico mentre depositi meteogenici (tufa), che si originano da acque di origine carsica a CO_2 prevalentemente biologica e/o atmosferica, sono frequenti nel settore adriatico.*
Le indagini geologico-stratigrafiche effettuate in seguito al terremoto del 1997 che ha colpito l'area del Colfiorito, hanno evidenziato la buona potenzialità dei travertini come strumento per indagini sulla tettonica attiva. E' risultata evidente una relazione diretta tra quota di affioramento ed età di formazione dei depositi; la differenza di età di formazione tra i depositi più orientali e quelli più occidentali, ha permesso di calcolare un tasso medio di sollevamento per questo settore della catena appenninica pari a 0.7 mm/anno.
I travertini sono anche sensibili indicatori delle variazioni che si verificano al momento della loro deposizione e, al loro interno, possono conservare testimonianze utili (polline, foglie, gasteropodi, ecc.) per le ricostruzioni ecologiche e climatiche. Indagini isotopiche ($\delta^{18}O$ e $\delta^{13}C$) e palinologiche, ancora in corso, in due depositi pleistocenici dell'Italia centrale (Serre di Rapolano e Tivoli) hanno fornito prime utili indicazioni per gli ultimi 120.000 anni. La buona corrispondenza tra i cambiamenti climatico/ambientali registrati dal polline e le fluttuazioni degli isotopi stabili dell'ossigeno e del carbonio facilita le correlazioni con gli eventi climatici già noti a scala regionale e globale. La potenzialità dei travertini come strumento per le ricostruzioni paleoclimatiche è rafforzata anche dalla constatazione che la maggior parte di questi depositi si sono particolarmente sviluppati durante le fasi interglaciali. Questa coincidenza sembra probabile: 1) in quanto la deposizione del travertino dipende dall'ammontare delle precipitazioni e 2) perché durante le fasi glaciali l'abbassamento del livello del mare è accompagnato anche dall'abbassamento del livello di base della circolazione carsica.

Keywords: Quaternary travertine, stable isotope, palynology, CO_2, neotectonics, paleoclimate, central-southern Italy.

Parole chiave: travertini quaternari, isotopi stabili, palinologia, CO_2, neotettonica, paleoclima, Italia centro-meridionale.

1 - INTRODUCTION

Travertine may have been among the first chemically formed stones after the initial cooling phase of the Earth and, among others, it could have represented a perfect environment for the development of the first living microbial on Earth (FARMER, 2000). Furthermore, in the re-cycling process to the atmosphere of "non volcanic" CO_2 from the Earth's interior, it also plays, especially along plate boundaries (BARNES *et al*., 1978), an important role in the global carbon cycle (BERNER *et al*., 1983). Having so many different shapes, textures, structures and colours, travertine is also an attractive stone, and this, along with its relative ease of quarrying and cutting, is the reason for its present commercial fortune as decorative building material.

Together with other countries of the Mediterranean region (i.e. Greece and Turkey), Italy is extremely rich in travertine s.s. deposits. Reasons for such abundance are the following:

1) the Mediterranean is an active plate boundary, with enhanced fluid motion at shallow levels in the crust, triggered by mantle-originated magmas and related thermal anomalies;
2) the Mediterranean region has thick Mesozoic pelagic and/or platform limestone sequences (formed in the Tethys ocean), often covered by thick impermeable flysch and syn-and-post-alpine clay-rich sedimentary sequences;
3) the Mesozoic limestone sequences, especially when buried by impermeable flysches and post-alpine sequences, may undergo (near orogenic granites and/or mantle magmas intruded in the crust) strong metamorphism and decarbonation in presence of hot, silica-rich solutions (skarn).

Acidic magmatic and/or metamorphic fluids, rising from depth, spread into the regional aquifer hosted in the high-permeable Mesozoic sequences, greatly enhancing the dissolution rate of the limestone. Related aquifer waters, eventually emerging at the surface as CO_2-rich, $CaCO_3$-oversaturated thermal springs ("soda springs"), quite often precipitate travertine at the edges of the limestone outcrops (MINISSALE, 2004 and references therein).

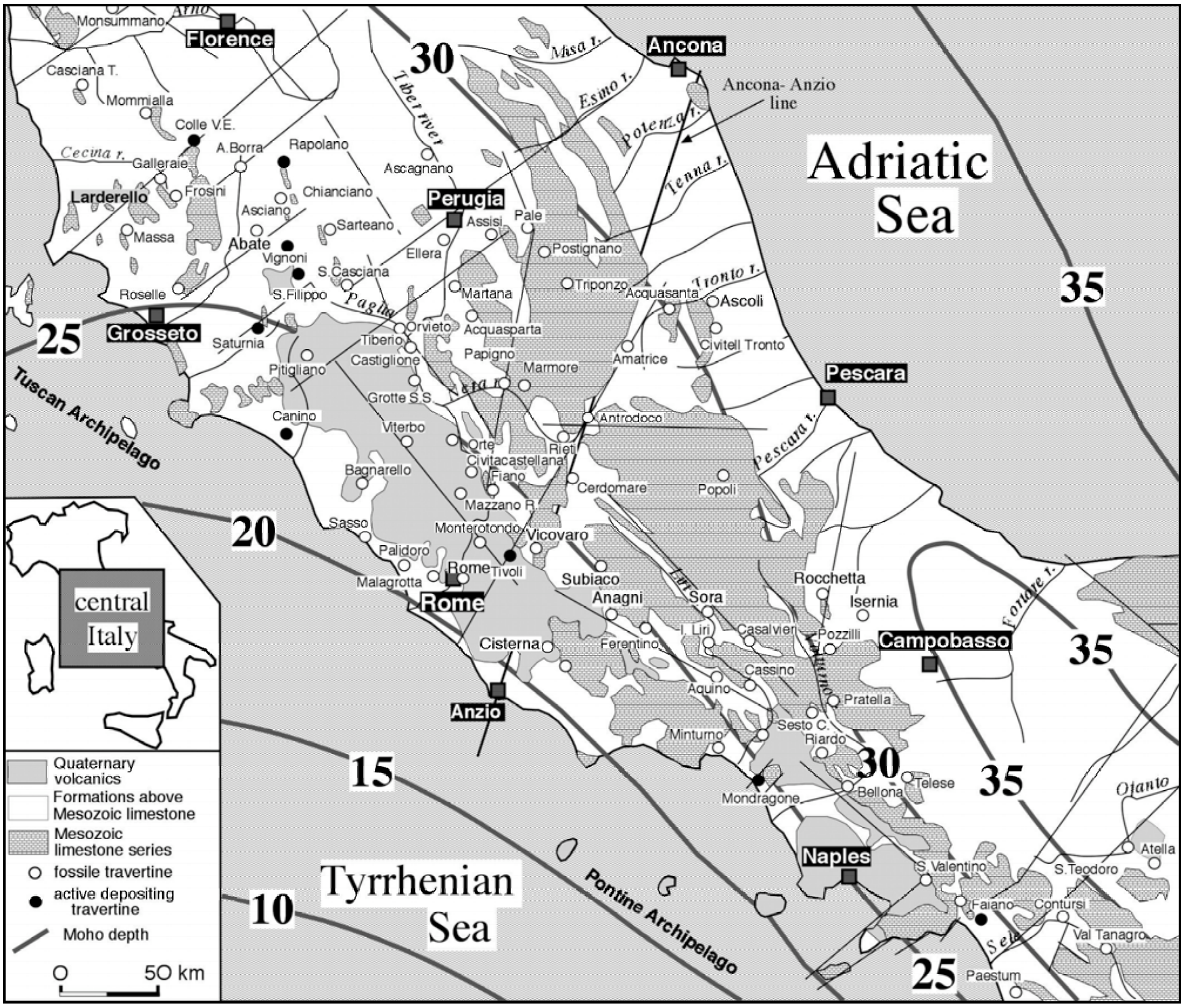

Fig. 1 - Active-precipitating and fossil travertine deposits in central-southern Italy (modified from MINISSALE, 2004).

I depositi di travertino attuali e fossili dell'Italia centro-meridionale (modificata da MINISSALE, 2004).

The entire western peri-Tyrrhenian coastal sector of central-southern Italy is affected by such thermal spring emergences, some of which still precipitate abundant travertine (Fig. 1), especially at the periphery of the active and Quaternary volcanoes. On the other side, widespread metheogene travertine deposits (tufa) formed (and are still forming) at higher elevations in the NW-SE trending inner central carbonate backbone of the Apennine Range. This type of travertine tends to be less compact and/or less diagenetically altered, with less pronounced stratification than travertine *s.s.*, reflecting a more turbulent regime of precipitating mother waters. The more metheogene character of such deposit, often directly precipitating from river falls, accounts for a different terminology, such as tufa (FORD & PEDLEY, 1996). A recent paper (ANDREWS, 2006) reviewed the paleoclimatic significance of such deposits in central-northern Europe for the last 13.000 ka.

In the present study the authors try to parallel the paleoclimate significance of travertine s.s. deposits of central Italy, with the one given by tufa, emphasizing also some genetic aspects, in terms of origin of CO_2 of mother solutions. Furthermore, being active and fossil travertine and tufa deposits of central Italy hosted in an extremely dynamic environment, their presence at different places, at different elevations, is tentatively related to the paleohydrology and the active tectonics of the last 500 ka.

2 - TRAVERTINE AS A PROSPECTING TOOL FOR THE GENESIS OF "MOTHER" CO_2

An active geothermal system, such as the Larderello geothermal field in Tuscany (Fig. 1), naturally generates, and moves to the surface, abundant deep, hot hydrothermal fluids. By limiting our attention simply on CO_2, the Larderello system transfers to the atmosphere, daily, about 3.000 tons of CO_2 (MINISSALE *et al.*, 2005). If this is the rate that can be directly measured (or estimated) in the natural steam vents and boiling pools ("Lagoni") located on top of the geothermal system, much more CO_2 probably escapes, laterally, from the cooler boundary condensation zones of the system (CECCARELLI *et al.*, 1987). Such CO_2 eventually enters the regional karstic hydrologic circuit(s) inside the regional carbonate reservoir, which at Larderello bounds extensively the geothermal system in its south-south eastern edges (Fig. 2, redrawn after MINISSALE, 1991).

On the other side, the Mesozoic carbonate sequences, which crop out as the main backbone of Italy, are huge collectors for meteoric waters topographically flowing, both westward and eastward, towards the Tyrrhenian Sea and the Adriatic Sea, respectively. Such descending waters, especially when intersecting the ascending geothermal CO_2 (and H_2S), dissolve the limestone in karstic circuits, greatly increasing the $Ca\text{-}HCO_3$ concentration of solutions, when compared if CO_2 derived only by organic, soil-derived CO_2 formed in the absorption areas. This double circulation pattern of CO_2 of different origin has been well documented in a large sector of central Italy, across the Tiber Valley, north of Rome (MINISSALE *et al.*, 2002).

The multiple origin(s) of CO_2 inside the Mesozoic limestone, and related effects on water-rock interaction processes during the cruise of CO_2 across the shallow crust, was already proposed by MINISSALE *et al.* (1997), which discriminated, in terms of $\delta^{13}C$ in CO_2, four main sources in central Italy:

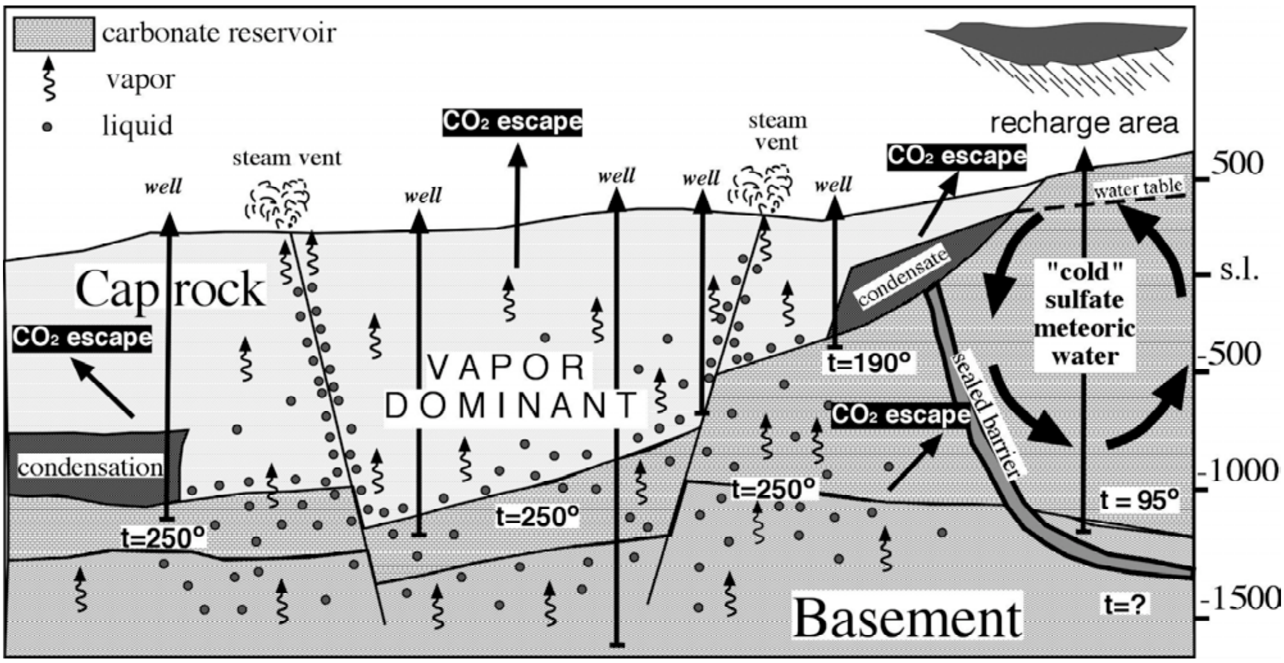

Fig. 2 - Conceptual section of the Larderello geothermal field in Tuscany (after MINISSALE, 1991) showing CO_2 patways from the geothermal system into the regional Mesozoic aquifer.

Sezione concettuale del campo geotermico di Larderello in Toscana (modificata da MINISSALE, 1991) che illustra la connessione tra le zone di produzione o di accumulo della CO_2, nonché il trasferimento di quest'ultima all'acquifero regionale nelle successioni carbonatiche Mesozoiche.

1) Atmospheric CO_2 in rainfall, with $\delta^{13}C$ value of about -7‰ PDB (ROLLISON, 1993).
2) Biogenic CO_2 from soil, entering into solutions during infiltration of meteoric waters; typically with $\delta^{13}C$ < -20‰ PDB (DEINES et al., 1974).
3) CO_2 deriving from the dissolution of carbonates during water-rock interaction, and typical of hydrothermal systems producing CO_2 with $\delta^{13}C$ around 0‰ PDB (ROLLISON, 1993)
4) Mantle CO_2: a large source of CO_2 at plate boundaries (BARNES *et al*., 1978) with $\delta^{13}C$ in the range -4 to -7‰ PDB (ROLLISON, 1993).

The relationship between the carbon isotopic composition of travertine and its mother CO_2 was well studied in the 1960's (CRAIG, 1963; FRITZ, 1965; GONFIANTINI *et al*., 1968; FRIEDMAN, 1970), and in the 1970's the $\delta^{13}C$-CO_2, as a prospecting tool for geothermal energy, in both gas vents, thermal springs and travertine, was proposed by PANICHI & TONGIORGI (1976). The latter, by measuring the carbon isotopic compositions of both precipitated travertine and exsolved CO_2 at 11 active travertine-depositing sites in central Italy, proposed an empirical relation given by the equation:

$$\delta^{13}C_{CO_2} = 1.2\ \delta^{13}C_{trav} - 10.5$$

to relate the $\delta^{13}C$ value of the dissolved CO_2 from travertine and the $\delta^{13}C$ value of the mother CO_2 promoting the pristine dissolution of limestone. Hereafter, all the travertine $\delta^{13}C$ discussed are not the values measured at the Mass spectrometer, but are the values recalculated according to the relation proposed by PANICHI &TONGIORGI (1976).

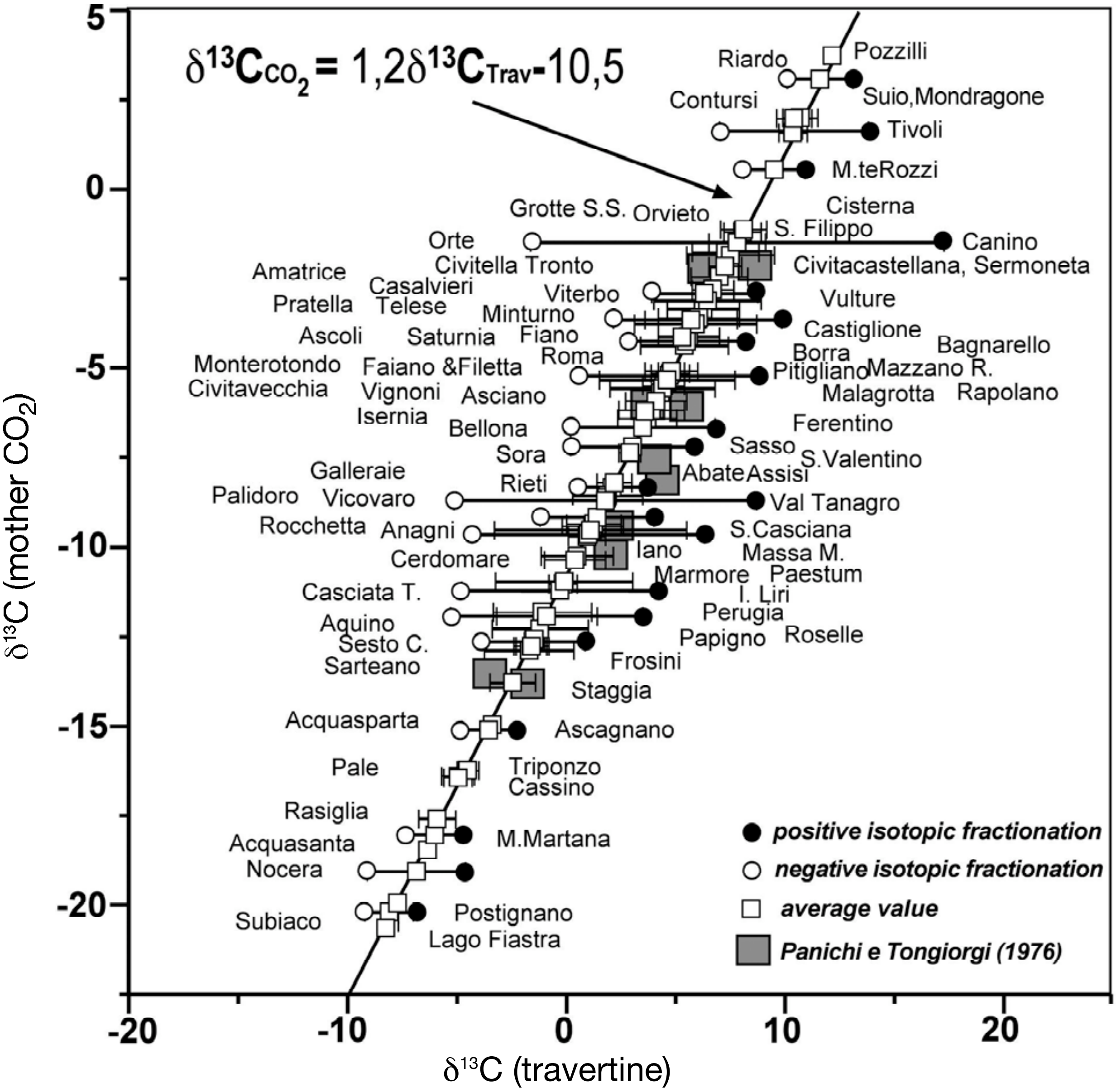

Fig. 3 - $\delta^{13}C$ of CO_2 vs. $\delta^{13}C$ in $CaCO_3$ from actively-depositing travertine areas (gray squares; data after PANICHI & TONGIORGI, 1976) and $\delta^{13}C$ values of CO_2 "recalculated" from $\delta^{13}C$ values of travertines according to the formula shown on top of the diagram. White and black circles refer to minimum and maximum measured $\delta^{13}C$ values in each travertine outcrop area plotted versus the average recalculated $\delta^{13}C$ of parent CO_2.

$\delta^{13}C$ della CO_2 vs. $\delta^{13}C$ in $CaCO_3$ per i travertini in formazione (quadrati grigi; dati in PANICHI & TONGIORGI, 1976) e per i travertini fossili in cui il $\delta^{13}C$ della CO_2 madre è ricalcolato da quello dei travertini, secondo la formula riportata nel diagramma. I pallini bianchi e neri si riferiscono rispettivamente ai campioni col minore e maggiore $\delta^{13}C$ per ciascun deposito.

Such isotopic data (most of which are from MINISSALE, 2004) are plotted in the $\delta^{13}C_{TRAVERTINI}$- $\delta^{13}C_{CO_2}$ diagram of Figure 3. Because of CO_2 fractionation effects during the flowing of mother waters in travertine precipitation pathways, the most negative $\delta^{13}C$ value of a single fossil deposit (open white circle in Fig. 3) represents the travertine formed near the emergence; the most positive (black dot) the more distal one. Travertine deposits plotting on the top right portion of the diagram are all located around active or Quaternary volcanic areas of central Italy; those in the bottom left are associated with the cold karstic springs, with value of $\delta^{13}C$ more negative typical of biogenic derived CO_2. The former (Fig. 1), prevalently locate in the western sector of Italy, have the typical massive appearance of thermogene travertine, the latter prevalently crop out in the intramontane areas of the Apennine Range (MINISSALE *et al*., 2002), having the appearance of tufa.

The cross comparison between data in Figure 3 and the geographical distribution of average re-calculated $\delta^{13}C$ in central Italy (Fig. 4), has two important implications: (1) the isotopic variability of carbon in the CO_2 sources is generally greater than the one induced by the fractionation during travertine deposition, as already suggested by the similar concentration of Sr in the relative springs and travertine deposits (MINISSALE, 2004), (2) both active and fossil travertine, being all of them younger than 500 ka (TADDEUCCI & VOLTAGGIO, 1987; FACCENNA *et al*., 1994; MINISSALE *et al*., 2002), derive by a regional hydrogeology that has not genetically changed much in the past 500 ka.

The briefly summarized relationship between: i) the isotopic composition of travertine, ii) mother CO_2, iii) structure and morphology of the Mesozoic limestone, in a similar hydrological pattern, implies that the carbon isotopic composition of a fossil travertine can be used as a prospecting tool for paleohydrology and for the presence of active and/or fossil geothermal and hydrothermal systems, as proposed by PANICHI & TONGIORGI (1976).

3 - TRAVERTINE AS INDICATOR OF ACTIVE TECTONICS

The possibility of deriving paleohydrology with travertine has important aspects related to tectonics. A clear relationship between surface discharge of deep, $CaCO_3$-oversaturated thermal fluids and active tectonics, was firstly pointed out by HANCOCK *et al*. (1999). In their study, based on observations in several Mediterranean areas, including some of the most well-known deposits, such as Tivoli in Italy and Pamukkale in Turkey, they proposed the use of travertine deposits as indicators of active tectonics. Here we discuss a case study in central Italy, where we have used the elevation of the travertine to calculate tectonic uplift rate, in connection with the fact that the hydrology (in terms of paleohydrology) within the Mesozoic carbonate aquifer, has reported in the previous paragraph, has apparently remained stable in the past 500 ka (MINISSALE, 2004).

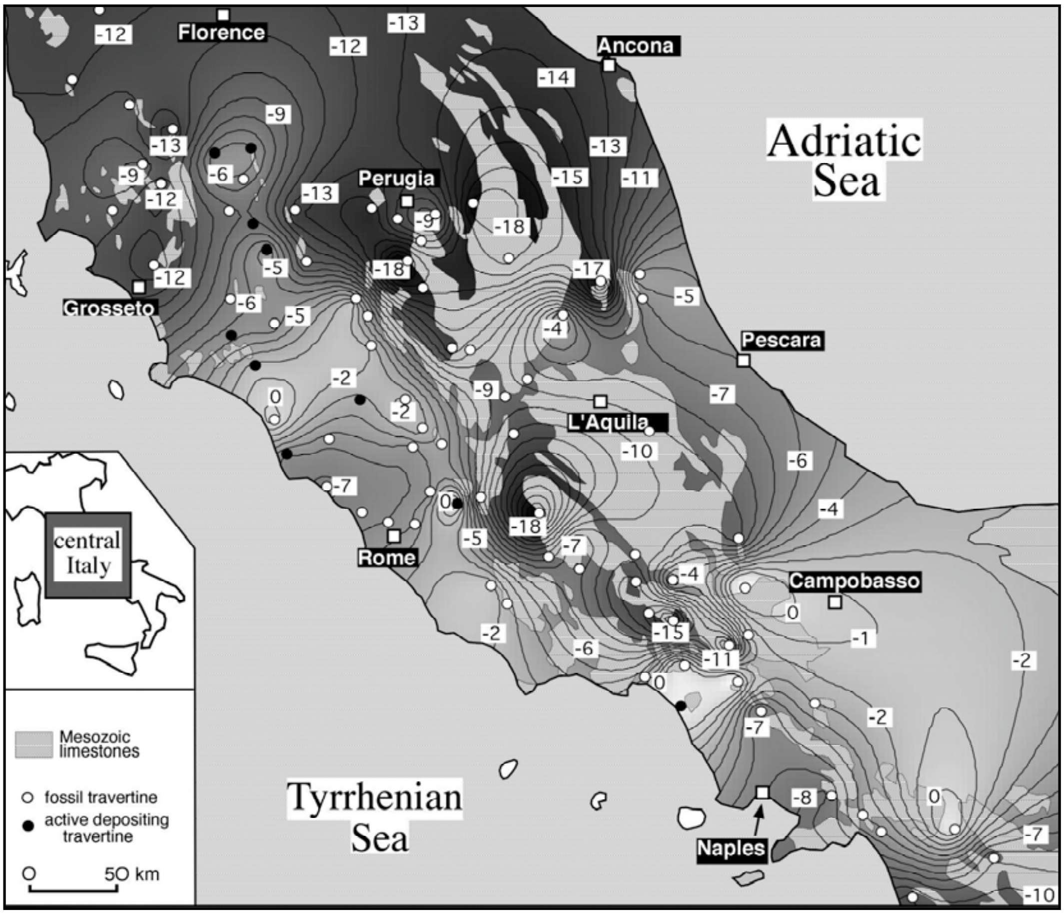

Fig. 4 - Iso-distribution map of recalculated $\delta^{13}C$ values of "parent" CO_2 of travertines; the figure shows more negative values in the inner parts of the Apennines suggesting CO_2 of prevalent biogenic (soil) origin with respect to isotopically heavier CO_2 of metamorphic origin along the peri-Tyrrhenian coast.

Mappa di isodistribuzione del $\delta^{13}C$ della CO_2 "madre" dei travertini: i valori più negativi si rinvengono all'interno della catena, suggerendo per questi un'origine meteogenica, rispetto a quelli tirrenici in cui la CO_2 ha un'origine più profonda.

During a recent study in the travertine outcrops centered in the Colfiorito area, and focused to find out relations between the earthquake occurred there in 1997 (CELLO *et al*., 2000) and the several active faults present in the area, all travertine deposits (Fig. 5) were sampled, among others, for $\delta^{13}C$ and $\delta^{18}O$ measurements, and several of them dated (PALADINI, 2005). By considering that: *i*) it has been taken as representative of the paleohydrology the highest elevation of each single deposit (most of these deposits are in narrow valleys, with sometimes large vertical drops); *ii*) samples for dating where chosen, when possible, from the centre of the deposit in well exposed walls; and *iii*) only samples appearing relatively unaltered were dated (MINISSALE *et al*., 2005). The most surprising result we obtained was to discover a strong positive correlation between the age of the single travertine deposits, their elevations, as well as their W-E geographical position inside the Apennine chain (Fig. 6). It is interesting to underlain that travertines located at present at an elevation of more than 800 m formed about 500 ka whereas travertines located at about 200-300 m are usually younger (or still active). It is also reasonable to suppose that old fossil travertine in the eastern sector of the Apennine, now located at high elevation, formed in the past when the base level of the karstic circulation, at that time, was at a much lower elevation.

According to several authors (e.g. BOCCALETTI & SANI, 1998), the Apennines in their intramontane inner sectors are still under strong compression, and still isostatically rising. According to the data shown in Figure 6, and supposing that the springs forming the travertine circulated in the same aquifer (i.e. the Mesozoic limestone), an average isostatic uplift rate of about 0.7 mm/year can be estimated for this sector of the Apennine Range. The uplift rate calculated in this way is in line with the ones estimated with other methods in other areas of

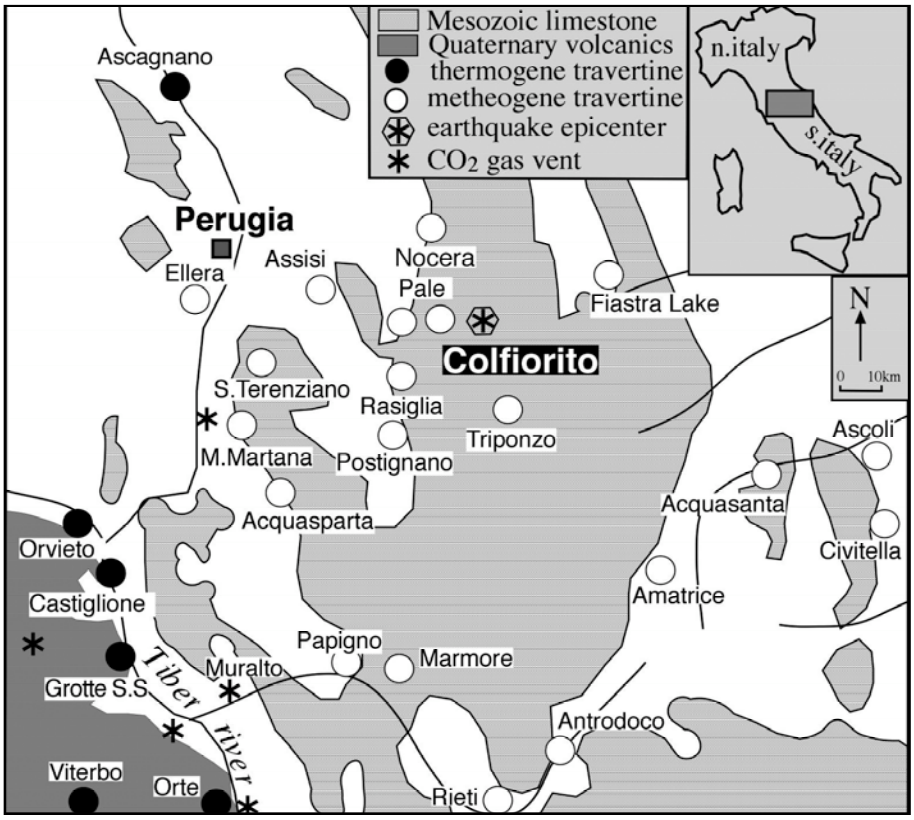

Fig. 5 - Geological sketch map of the 1997 Colfiorito earthquake area in central Italy with location of the main travertine outcrops nearby.

Mappa geologica dell'area del Colfiorito (Italia centrale) interessata dal terremoto del 1997 con l'ubicazione dei principali affioramenti di travertino.

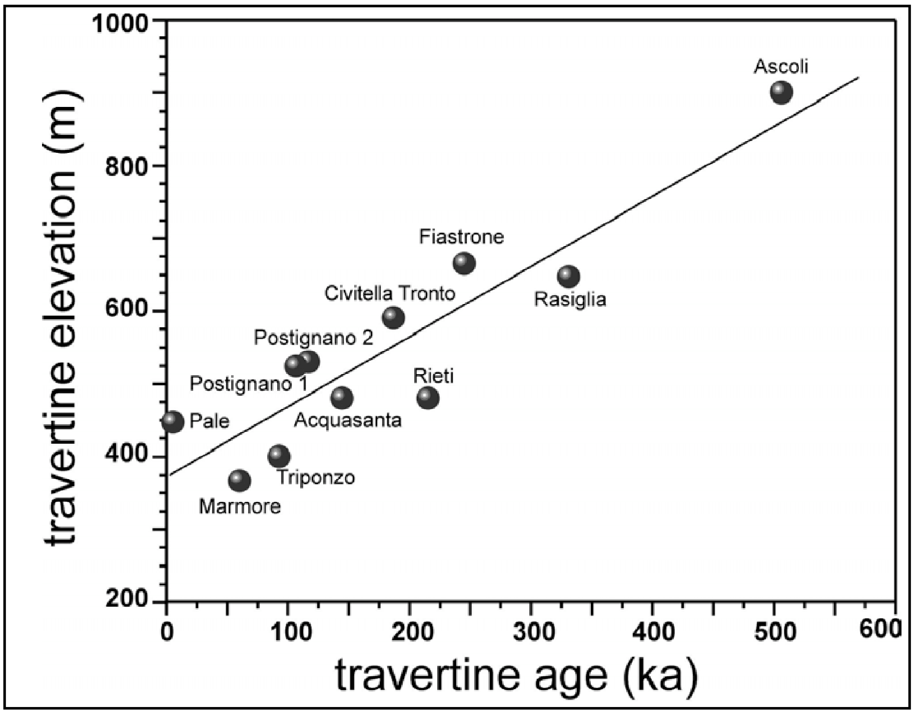

Fig. 6 - Diagram of elevation versus age of travertine outcrops in the Colfiorito area in central Italy (MINISSALE *et al*., 2005); from the diagram an isostatic rising spead of 0.7 mm/y can be calculated for this part of the Apennines.

Diagramma di correlazione tra quote ed età dei travertini che affiorano nell'area del Colfiorito in Italia centrale (MINISSALE et al., *2005); dal diagramma si evidenzia un tasso di sollevamento per la catena appenninica di 0.7 mm/anno.*

the Apennines, such as 0.4 mm/year using fission tracks (Balestrieri *et al*., 1996), and 0.2-0.7 mm/year using vertical fault slip rates (Bonini *et al*., 2003).

4 - TRAVERTINE AS PALEOCLIMATE PROXY

Although its potentiality is not well assessed yet, travertine could also be a very important proxy for paleoclimate reconstructions. In fact, it is reasonable to suppose that the $\delta^{18}O$ of CO_3-ions in precipitated travertine might depend upon the $\delta^{18}O$ of the ocean, via the isotopic composition of "mother" rainfalls entering the karstic circuits. More positive $\delta^{18}O$ values are found in interglacial periods. This relation has been recently reviewed for tufa deposits in northern Europe (Andrews, 2006). What is peculiar with travertine is that the study of the variation of the $\delta^{13}C$ of CO_3-ions, could give light on the contemporary origin of CO_2 inside the deep aquifer, and its proportion with atmospheric CO_2, as suggested in the previous paragraphs.

Other isotopic compositions (e.g. $\delta^{35}S$, $\delta^{87}Sr$, $\delta^{208}Pb$) and the concentration of some minor and trace elements of travertine (e.g. Mg and Sr), can also be useful indicators of climate-driven changes (Sturchio *et al*., 1992; Dramis *et al*., 1999). In the same perspective: incorporated pollen, aerosols, microbes, plant and animal macro-remains, and other organic matter, might all be potential indicators of environmental conditions. As a matter of fact, all these potentialities can be developed by applying precise age determinations, such as the U-series method (Sturchio *et al*., 1994; Frank *et al*., 2000; Matsuoka *et al*., 2001) to the denser layers of pure travertine, if they are younger than ca 500 ka.

Minissale *et al*. (2005) published 30 dates from the main travertine outcrops of central Italy which, along with dates from the literature, provided an opportunity to compare periods of active travertine deposition with climatic cycles, obtained on a global scale with other proxies (e.g. Martinson *et al*., 1987). As shown in Figure 7, a good agreement between interglacial warm periods and the travertine deposition rates, at least for interglacials 1, 3, 5 and 7 is evident. The agreement is particularly striking if we consider that the sampling criteria for dating travertine deposits in central Italy, was essentially random. The fact that some travertine dates correspond with glacial periods (e.g. two samples in glacial 4 and three in glacial 6), means that, in glacial periods, the precipitation of travertine was not entirely absent, but was probably reduced.

Because precise correspondence between isotopic fluctuations in travertine and climatic parameters in central Italy has not been verified yet, investigations in the last years on stable isotopic compositions ($\delta^{18}O$, $\delta^{13}C$) and palynological analyses in two Pleistocene sites (Serre di Rapolano - Siena, and Tivoli - Rome; Bertini *et al*., 2007; Ricci, 2007; Ricci *et al*., 2007) were carried out. What we obtained at Serre di Rapolano is summarized below.

At Rapolano (Fig. 1 for location), three different sites (Alibrando-Dei=AD, Filicheto=F and Le Querciolaie=LQ) have been selected and sampled for both palynological and stable isotopic analyses. The relative sections and stratigraphic profiles, including the 13.5 m core at LQ, are shown in Figure 8.

In order to better evaluate the taphonomic biases affecting the pollen content in travertines - an uncommon lithology for palynological studies - samples were collected from: i) different travertine lithotypes (e.g. crystalline crust, shrub, lithoclastic), ii) terrigenous interstrata and iii) paleosoils. Taphonomic biases have also been assessed in samples from surface water and soft bottom sediment, from a small pool where travertine precipitates nowadays (Borro Canatoppa) (Fig. 9). Samples from Musci were also taken next to the pool edge.

Preliminary data, summarized in Figures 10-12, document the main floristic, vegetational and climatic changes observed. Sixty-nine pollen morphotypes have been identified, at the family and generic levels. They have been referred to twenty-seven arboreal (e.g. *Pinus, Carpinus, Quercus, Ulmus, Tilia*) and to thirty-eight non arboreal (e.g. Poaceae, Asteraceae, Chenopodiaceae, Cyperaceae, Sparganiaceae) taxa. *Pseudoschizaea sp.*, Pteridophyta and Fungi have also been detected. With the exception of sparse pollen grains of *Taxodium*, *Myrica* and *Engelhardia* in the AD section, taxa more typical of pre-Pleistocene are absent. Among Pinaceae, largely dominated by *Pinus, Cedrus* is continuously present, whereas *Tsuga* is more scattered.

The most encouraging result of

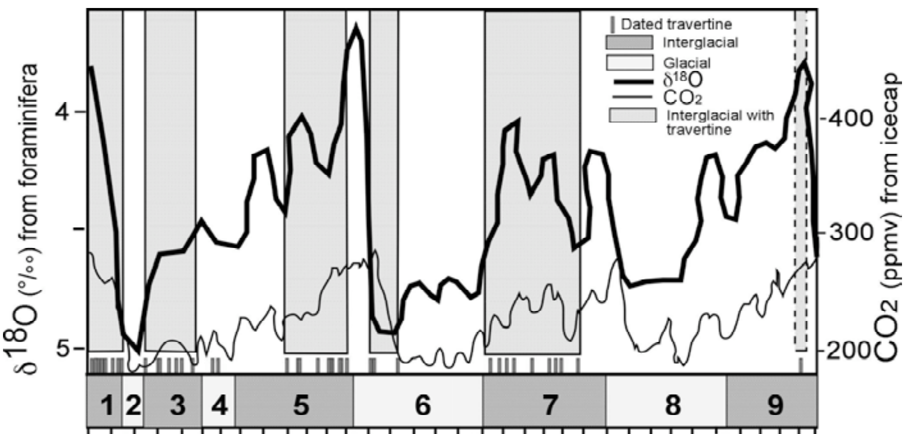

Fig. 7 - Climatic cycle variations for the past 340 ka derived from the $\delta^{18}O$ of the ocean as registered in the tests of benthonic foraminifera (thick black line) and the CO_2 concentration of the atmosphere (thin line) as registered in ice core samples (redrawn after Paillard, 1998; Petit *et al*., 1999; Shackleton, 2000). Singles dated travertine are shown in the lower part of the diagram.

Cambiamenti climatici durante gli ultimi 340 ka registrati nel record biostratigrafico e isotopico ($\delta^{18}O$) dei foraminiferi bentonici (linea nera spessa) e nella CO_2 intrappolata nei ghiacci delle calotte polari (linea sottile) (ridisegnato da Paillard, 1998; Petit et al., *1999; Shackleton, 2000). I singoli travertini datati sono segnati nella parte bassa del diagramma.*

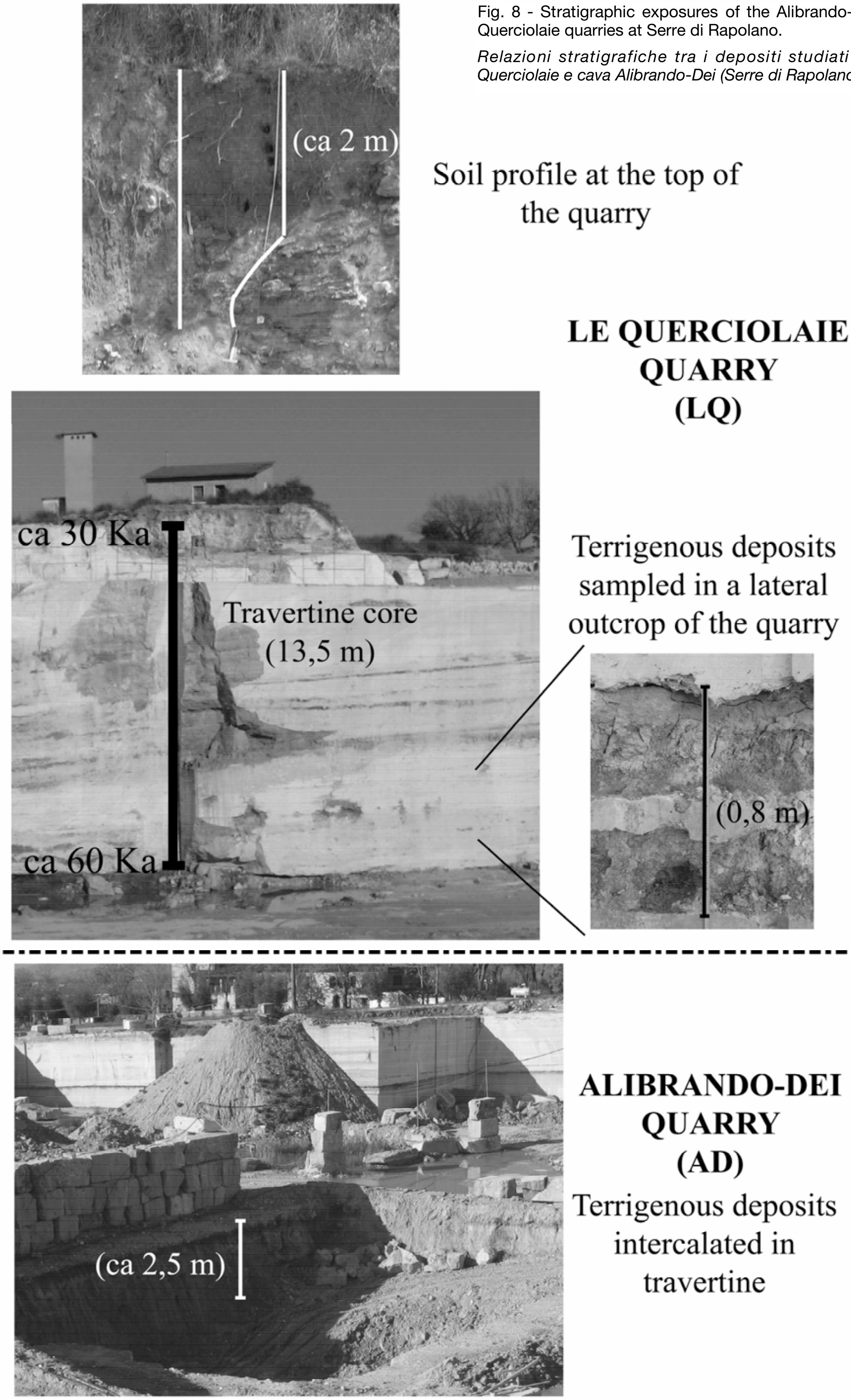

Fig. 8 - Stratigraphic exposures of the Alibrando-Dei and Le Querciolaie quarries at Serre di Rapolano.

Relazioni stratigrafiche tra i depositi studiati a cava Le Querciolaie e cava Alibrando-Dei (Serre di Rapolano).

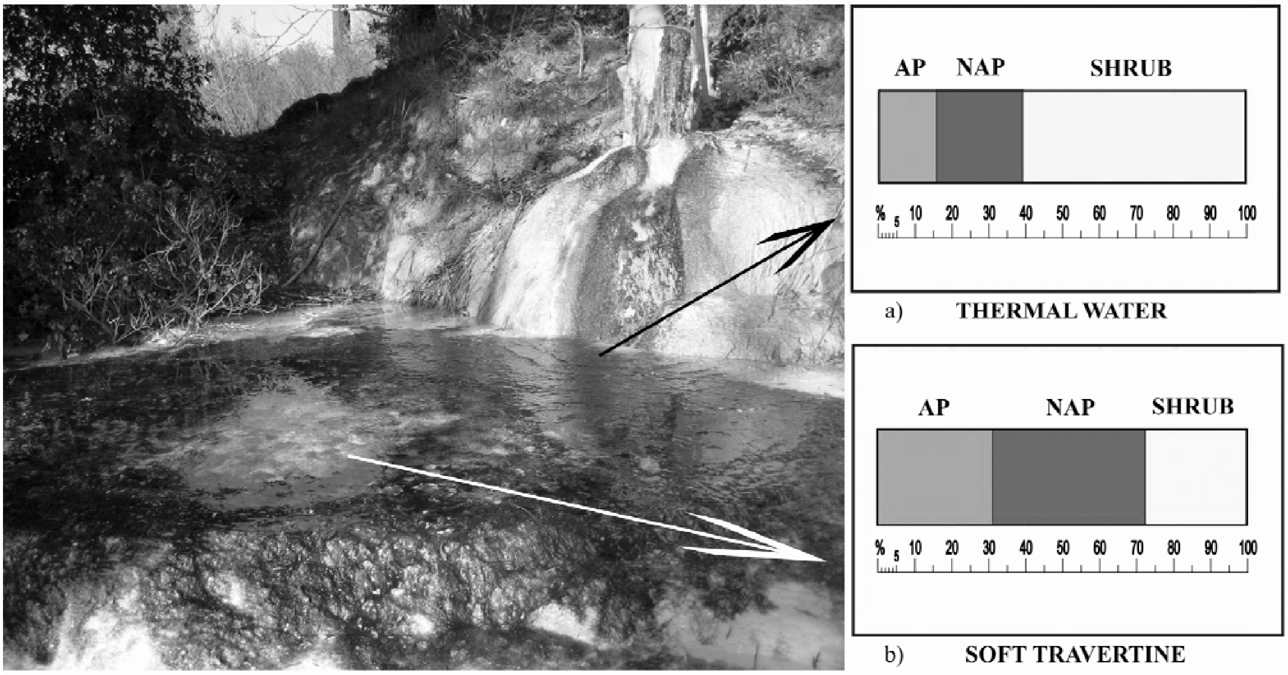

Fig. 9 - Borro Canatoppa thermal water near Serre di Rapolano. Local plant species are largely represented in the summary pollen spectra from: (a) the $CaCO_3$ saturated thermal water, and (b) the related soft sediment precipitating at the bottom of the pond. The bordering vegetation (mainly Araliaceae, included in the shrubs) is reflected, especially in the pollen spectrum (a), clearly marked by a dominant seasonal input too. The difference in percentage between (a) and (b), possibly is also related to destruction of palynomorphs during diagenesis.

Pozza di acqua termale in prossimità del Borro Canatoppa vicino a Serre di Rapolano. Gli spettri pollinici relativi all'acqua termale superficiale (a) e al travertino appena deposto sul fondo della pozza (b) mostrano una generale dominanza della componente pollinica locale. Nello spettro pollinico dell'acqua termale (a) risulta inoltre marcata anche la componente stagionale (Araliaceae - arbusti), molto meno evidente nello spettro (b) nel quale le associazioni polliniche risultano dall'accumulo di polline lungo più stagioni. Le differenze nei valori percentuali tra gli spettri (a) e (b) sembrano inoltre essere legate anche agli effetti di distruzione selettiva durante la fase di diagenesi.

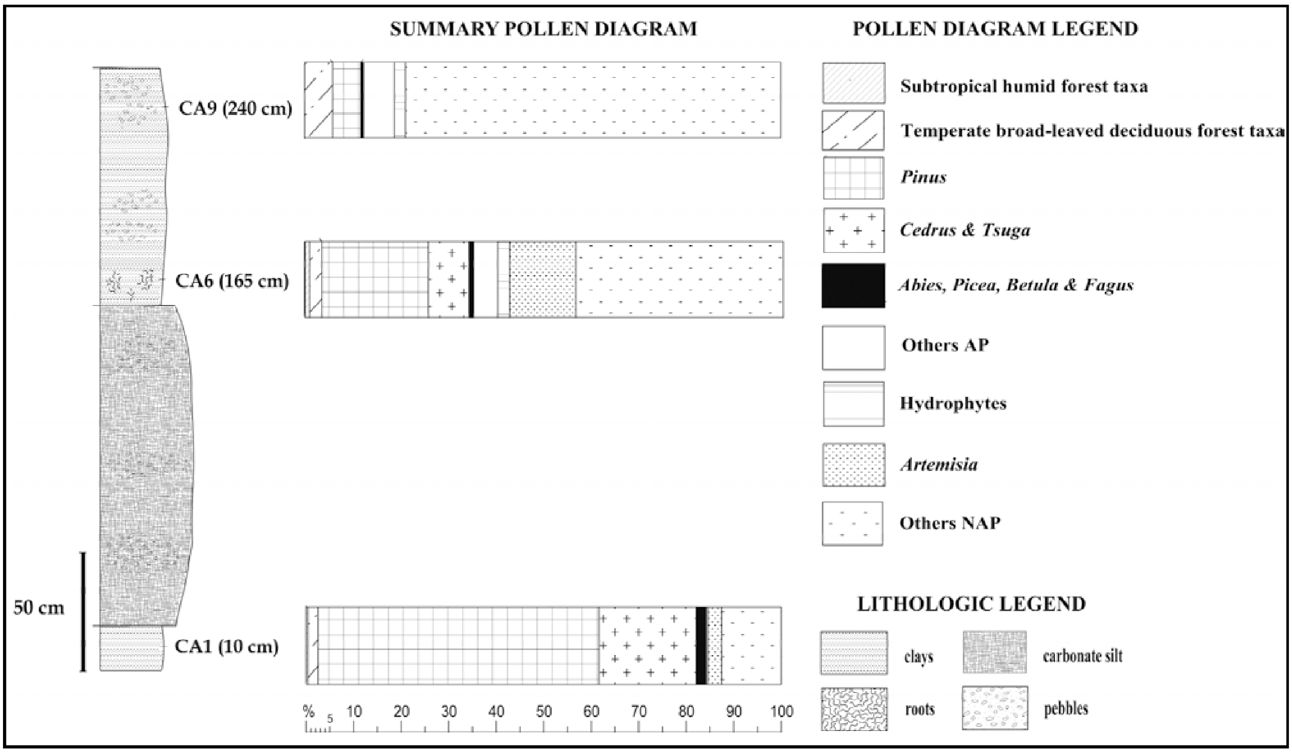

Fig. 10 - Alibrando-Dei quarry: summary pollen diagram. Pollen of arboreal plants (AP) is dominant (85%) in the basal sample (CA1); AP consists prevalently of Pinaceae, especially *Pinus* followed by *Abies* and *Cedrus*; deciduous forest taxa are subordinate (always below 2%). Herbs (about 15%) include: Asteraceae, Poaceae, Chenopodiaceae; they progressively increase in the overlaying samples, reaching a maximum of 80% in CA9. *Artemisia* shows a peak in the CA6. Scanty pollen grains of *Engelhardia, Taxodium* and *Myrica* have been also detected.

Cava Alibrando-Dei: diagramma pollinico sintetico. Nel campione alla base (CA1) domina il polline delle piante arboree (AP) (85%); queste sono prevalentemente costituite da Pinaceae, soprattutto Pinus *seguito da* Abies e Cedrus*; i taxa arborei decidui sono sempre in percentuali inferiori al 2%. Le erbacee (Asteraceae, Poaceae e Chenopodiaceae; ca 15%), aumentano progressivamente nei campioni sovrastanti raggiungendo percentuali massime pari all'80% (CA9).* Artemisia *ha un picco nel campione CA6. Presenti anche rari granuli pollinici di* Engelhardia, Taxodium e Myrica.

this survey is the discovery of clearly distinct pollen assemblages, recording different paleoenvironmental and paleoclimatic conditions. The pollen record allows also discrimination between local and regional events (Figs. 10-12). The local one, as pointed out at the base of LQ, is mainly testified by the development of herbaceous vegetation, typical of wetlands (i.e. marshes); the regional one, by the expansion of steppe taxa, especially *Artemisia* (e.g. at Filicheto and in CT14 of LQ), or arboreal taxa such as *Pinus* and *Quercus* (sample CT9 of LQ). Regional events possibly correspond to climatic changes correlative with stadial/interstadial fluctuations.

Comparison between pollen and isotopic data is complicated by the fact, sometimes, that the more compact lithotypes formed near the orifice (e.g. crystalline crust formed in slope; Guo & Riding, 1998) have low pollen concentration. In spite of this, data presented here, suggest a quite good correlation between the isotopic and the pollen fluctuations in the LQ core. A parallel increase of $\delta^{18}O$ values (up to ca 2,5‰), and percentages of arboreal pollen (Pinaceae and temperate broad-leaved deciduous temperate taxa) has been recorded in the middle portion of the core (Fig. 11).

According to the nine radiometric ages provided by Bellucci (2007), the LQ core is supposed to cover a time interval between ca 60 and 30 Ka, partly coinciding with the Middle Weichselian and the Marine Isotopic Stage 3. At Rapolano, during this time interval, the wide expansion of herbaceous plants (including *Artemisia*) suggests the presence of open landscapes, indicative of cold and dry conditions. However a relatively more humid and warm phase is testified by the increase of the arboreal plants in correspondence of the central portion of LQ core. The sporadic presence of *Engelhardia, Taxodium* and *Myrica* in the AD profile (Fig. 10), if not due to reworking, could be indicative of a long hiatus among the AD and the LQ core. If the age of the upper part of LQ core is at 30 Ka, the large expansion of thermophilous taxa, indicative of warm

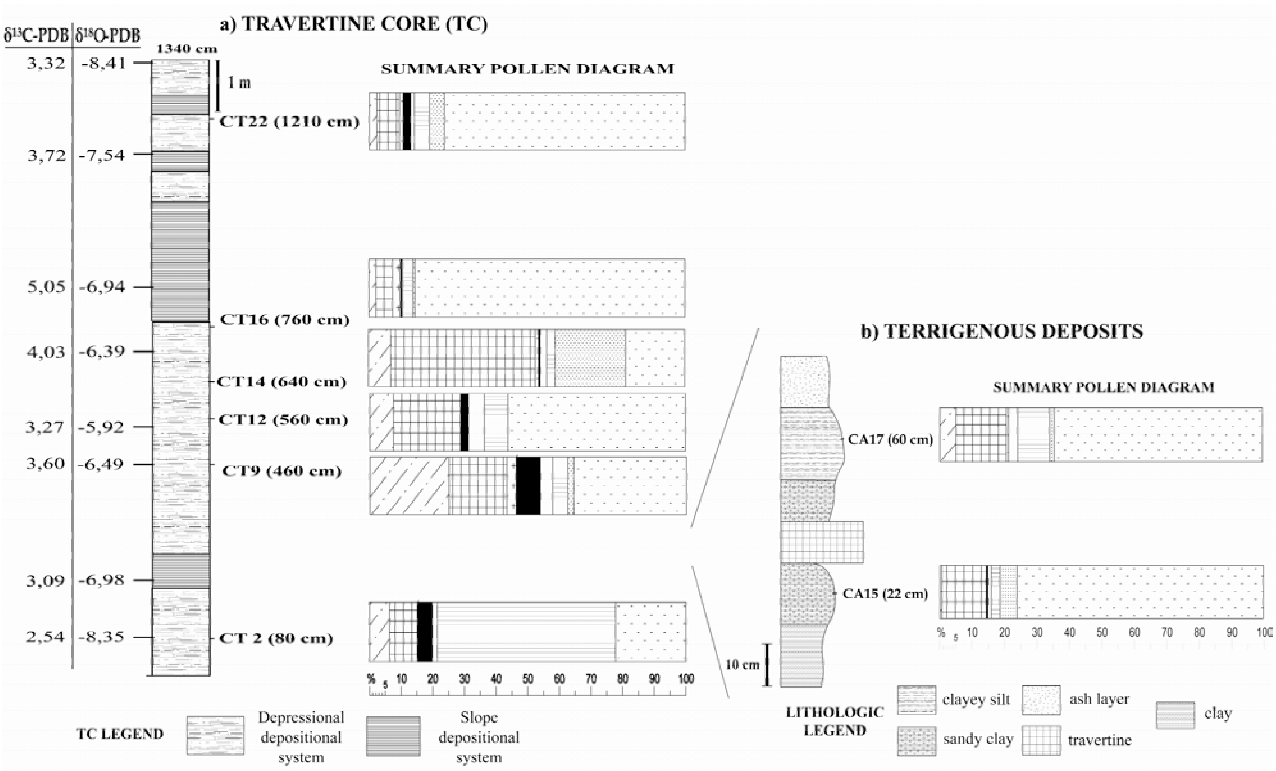

Fig. 11 - Le Querciolaie quarry. a) Summary pollen diagram of the travertine core (TC) retrieved and previously studied for $\delta^{13}C$, $\delta^{18}O$ and U/Th datation by Bellucci (2007); on the left isotopic data (Ricci, 2007). b) Summary pollen diagram from the terrigenous deposits intercalated within TC. For the legend of the pollen diagram see Figure 10. A dominant edaphic signature is well expressed by the large occurrence of Cyperaceae at the bottom core (CT2). CA15 and CA17 contain abundant herbaceous pollen grains, but within hydrophytes are strongly reduced. A good expansion of temperate broad-leaved deciduous forest taxa is testified in sample CT9; here Pinaceae also increases, especially *Pinus*, followed by *Cedrus* and *Abies*; then herbs increase again, reaching maximum values in CT16 (88%) and CT22 (ca 80%), with Poaceae and Asteraceae Asteroideae. A good expansion of *Artemisia* is recorded at the same time of an increase of Pinaceae in CT14.

Cava Le Querciolaie. a) Diagramma pollinico sintetico della carota di travertino (TC) prelevata e studiata ($\delta^{13}C$, $\delta^{18}O$ e datazioni U/Th) da Bellucci (2007); sulla sinistra sono riportati i valori isotopici del carbonio e dell'ossigeno (Ricci, 2007). b) Diagramma pollinico sintetico dei depositi terrigeni intercalati a TC. Per la legenda dei diagrammi palinologici si veda la Figura 10. Un forte segnale edafico è rappresentato dalla marcata presenza di piante acquatiche (Cyperaceae) nella parte basale della carota (CT2). Nei campioni CA15 e CA17 sono ben documentate le piante erbacee mentre le idrofite sono fortemente ridotte. Una buona espansione dei taxa di foresta temperata è testimoniata nel campione CT9; qui aumentano anche le Pinacee, prevalentemente Pinus*, seguito da* Cedrus *e* Abies*. Nei campioni soprastanti le erbacee aumentano di nuovo (Poaceae ed Asteraceae Asteroideae), raggiungendo i valori più elevati in CT16 (88%) e CT22 (80%). Nel campione CT14 si osserva una buona espansione di* Artemisia *e Pinaceae.*

and humid conditions, found at the very top of LQ grading into the surface soil (Figs. 8 and 13), could be related to some later Pleistocene interstadials or the Holocene. The dominance of Asteraceae in the soil is clearly related to the usual pedogenic processes.

5 - CONCLUSION

Italy (more generally the entire Mediterranean region) with the large number of extensive limestone outcrops and frequent thermal anomalies associated to active volcanism, is an ideal place for travertine formation.

As proposed by PANICHI & TONGIORGI (1976) in a pioneering paper, travertine is a powerful tool for geothermal energy prospecting. On the other side, the $\delta^{13}C$ values of travertine can be also used to trace the source of CO_2 (e.g. atmospheric, biogenic, hydrothermal, mantle) and relations with underground water-gas-rock interaction processes (MINISSALE *et al*., 2002).

More than this, travertine can be used also as a powerful tool for investigate active tectonics (HANCOCK *et al.*, 1999) and, as presented in this study, to calculate the average rising speed of an active orogen, such as the central-southern Apennines. Such a relation, constrained by the reasonable hypothesis that the circulation paths inside the Mesozoic limestone have remain stable in the last 500 ka, can also be used to trace the paleohydrology of central-southern Italy.

In terms of potentiality for paleoclimate reconstructions, the parallel stable isotopic ($\delta^{18}O$, $\delta^{13}C$) and palynological analyses carried out in two Pleistocene travertines of central Italy, i.e. Serre di Rapolano (Siena) and Tivoli (in progress), allowed to investigate the last ca 120 kyrs. The observed environmental fluctuations at both sites demonstrate that travertine deposits, can be used, such as tufa, to investigate the paleoclimate of the late Quaternary. Detailed palynological studies are still in progress, they will facilitate a closer comparison with other terrestrial (e.g. Monticchio, ALLEN *et al.*, 2000; Valle di Castiglione, FOLLIERI *et al*., 1988; Lagaccione, MAGRI, 1999), ice-core, as wells as deep-sea (e.g. MARTINSON *et al*., 1987; DANSGAARD *et al*., 1993; GROOTES *et al*., 1993; BOND *et al*., 1993) records. In line with this interpretation, is the already described observation that most dated travertine in central Italy cluster in intergla-

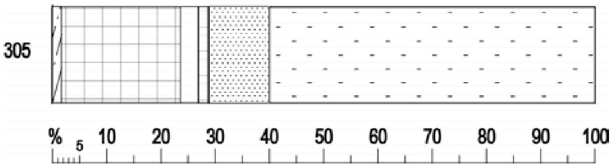

Fig. 12 - Filicheto quarry: summary pollen diagram (for the legend of the pollen diagram see figure 10). This single sample was collected to have taphonomical information on the pollen content in a less compact and more altered lithotype. Herbs (73%), including Poaceae, Asteraceae (with *Artemisia* at 11%) and *Plantago*, dominate. Among the arboreal plants *Pinus* is the most abundant component.

Cava Filicheto: diagramma pollinico sintetico (per la legenda del diagramma palinologico si veda la Figura 10). Il campionamento palinologico di questo livello di travertino è giustificato dalla necessità di ottenere informazioni tafonomiche da litotipi poco compatti e alterati. Dominano le erbacee (ca 73%), come Poaceae, Asteraceae inclusa Artemisia *(11%) e* Plantago*. Tra le piante arboree* Pinus *è il componente principale.*

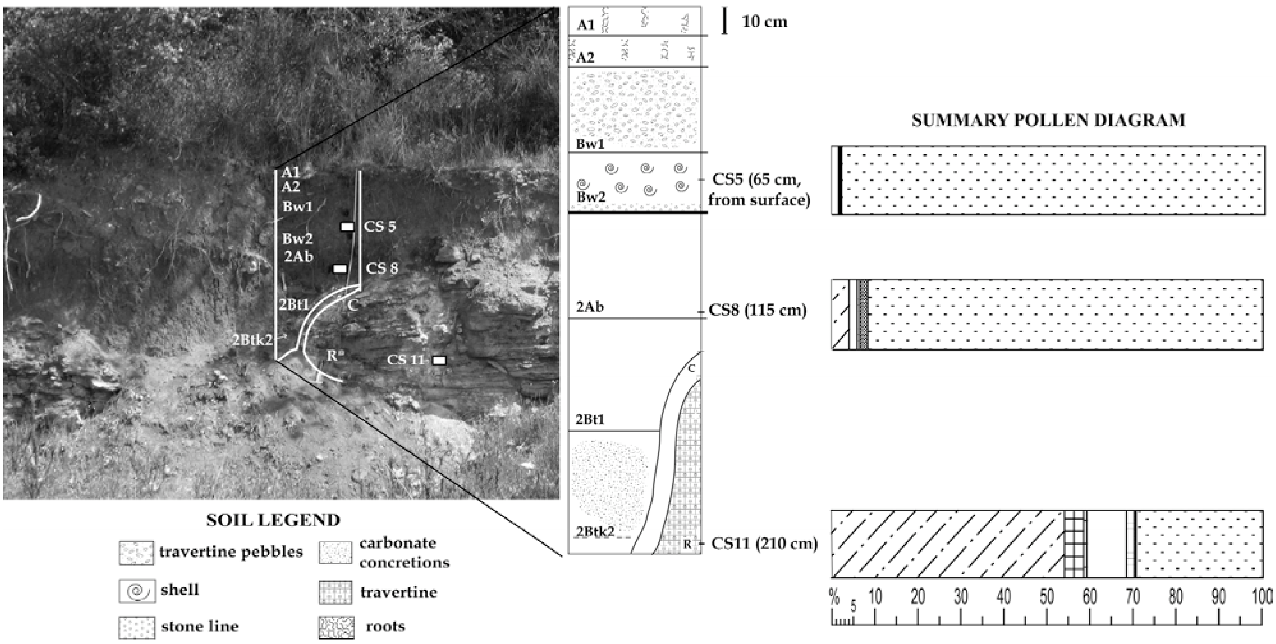

Fig. 13 - Soil profile at the top of Le Querciolaie quarry: summary pollen diagram (for the legend of the pollen diagram see Figure 10). With the exception of the basal sample (CS11) where pollen from arboreal plants is abundant (ca 70%), pollen spectra from the soil are dominated by herbaceous plants (Asteraceae Cichorioideae).

Suolo al tetto di cava Le Querciolaie: diagramma pollinico sintetico (per la legenda palinologica si veda la Figura 10). Ad eccezione del campione basale prelevato nel travertino (CS11), dove il polline delle piante arboree è abbondante (ca 70%), i campioni prelevati nel suolo sono dominati da erbacee come Asteraceae Cichorioideae.

cial periods. And this seems reasonable for two reasons: 1) because the deposition of travertine is depending upon rainfall amounts, and 2) because in glacial periods, the lower level of the oceans also lowers the base level of karstic circulation.

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