Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, 2010
Πρακτικά 12ου Διεθνούς Συνεδρίου
Πάτρα, Μάιος 2010

Bulletin of the Geological Society of Greece, 2010
Proceedings of the 12th International Congress
Patras, May, 2010

INVESTIGATION OF THE FORMATION OF SPELEOTHEMS IN THE AGIOS GEORGIOS CAVE, KILKIS (N. GREECE)

Antonelou A.[1], Tsikouras B.[1], Papoulis D.[1], and Hatzipanagiotou K.[1]

[1] *University of Patras, Department of Geology, Section of Earth Materials, 26500 Patras, Greece, antonelou@upatras.gr, v.tsikouras@upatras.gr, papoulis@upatras.gr, k.hatzipanagiotou@upatras.gr*

Abstract

The Agios Georgios cave at Kilkis (North Greece) contains a large variety of speleothems and it is considered as one of the most decorated caves of Greece. For this study a coordinated geochemical and textural investigation of the speleothem was carried out. This stalactite was cut along its growth axis and a transverse slab of it shows parallel calcite layers of varying thickness and colour, whose regularity and spacing suggest an annual origin. Microscopic investigation of polished-thin sections resulted in a detailed description of several fabric types. Scanning Electron Microscopic study and microanalyses revealed that pure calcite is dominant; local Mg-bearing calcite occurs, too. In some pores among the faceted crystals there is a variety of clay minerals that, along with the development of Mg-bearing calcite, are interpreted as the result of microbiological or/and climatic changes. Numerous changes in environmental conditions in caves (particularly changes in water flow rates) cause variations in the degree of perfection of crystallite lateral growth and inclusions may trapped by their advancing growth surface. The speleothem is studied in order to generate archives of climate change (aridity, flow rates etc.) and indentifying shifts in climate system. The successive laminae in the studied speleothem from Agios Georgios suggest alternative cool and warm periods in the past climatic conditions of northern Greece.

Key words: *speleothems, microfabrics, Agios Georgios Cave, North Greece.*

1. Introduction

Caves are formed by different processes in many rock types and unconsolidated sediments. They can be classified according to their origin and the lithology of host rock or the type of sediment (Ford and Williams, 1989). The most common type of caves is limestone dissolution cave, which forms as a slightly acidic fluid (carbonic acid) erodes the limestone. Caves that form in this way can be very deep and contain substantial number of chambers or rooms. Chemical reactions under these very precisely controlled conditions permit the growth of unusual minerals and the growth of crystals of exceptional size. Mineral deposits take on the form of stalactites, stalagmites, flowstones, and other forms known collectively as speleothems. Because these deposits are nourished by water seeping down from the surface, changes in the climate and vegetation on the surface leave their signatures in the growth bands of the speleothems. The deposits of caves have become an important source of paleoclimatic information (e.g. Fairchild et al., 2006). Use of cave speleothems has been proven to be a powerful tool for the study of past climate and environmental changes. The noteworthy properties of climate recording by these cave formations result from their mineralogy and fabric, as well as from their mode of occurrence (Bertaux et al., 2002). Similar to corals, tree rings, annual laminations in maar lakes and annual layers in ice cores speleothems may present an annual and subannual laminate that can be used

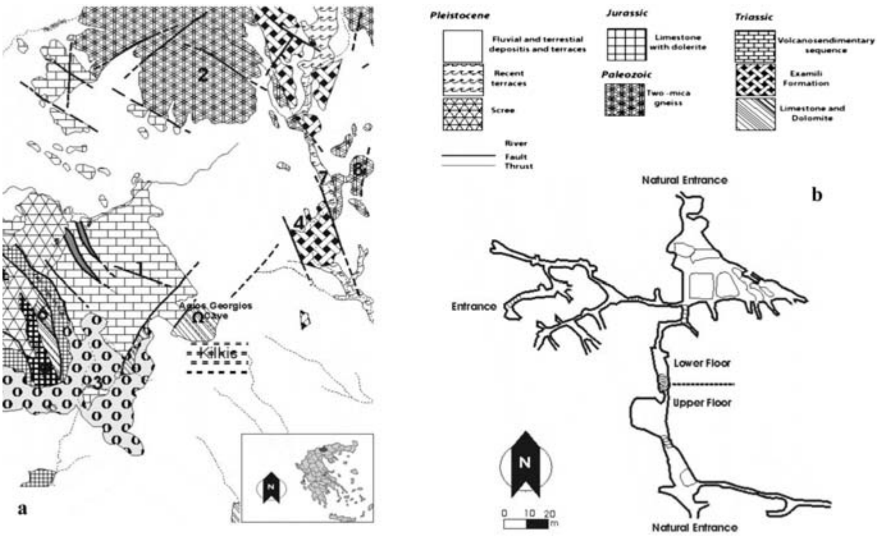

Fig. 1: (a) Geological map of broader area of Kilkis (after Kockel and Ioannides, 1979) Ω: Agios Georgios cave (b) Map of Agios Georgios cave (mapping from Hellenic Speleological Society).

in studies of climate reconstructions (Genty and Quinif, 1996; Kaufman et al., 1998; Baker et al., 2008).

The aim of this study is to present a detailed description of the fabrics present in a 181mm long stalagctite from the Agios Georgios Cave, Kilkis, N. Greece, to relate their development to different climatic conditions and to suggest possible climatic changes that have been imprinted in the speleothem texture. Interpretation of fabrics and the collected data serve to demonstrate that the petrographic characteristics may have recorded a climate signal.

2. Geological and Speleological Setting

The Agios Georgios cave (Latitude 40°59'32''N; Longitude22°52'20''E) is located at the south-west of Agios Georgios hill in Kilkis (47 km north of Thessaloniki, Greece), Central Macedonia Valley. It is a limestone cave developed in the limestone with local dolomite of Middle- Upper Triassic part of Deve-Koran Sequence (Kockel and Ioannides, 1979) (Fig. 1a) which belongs to the circum Rhodope zone (Kaufmann et al., 1976).

The Agios Georgios cave has an extent of 1000m^2 with a visiting path about 500m long. The cross-like pattern is developed in east-west and south-north directions (Fig. 1b). It has two natural entrances the northern, at the lower level and the southern at the upper level; both of them are blocked from aggregates. The passages are narrow and high, looking like clefts. Most of them have a north-south or an east-west direction, obviously depending on the direction of tectonic structures in the limestone. The Agios Georgios cave is developed in the "upper floor" and the "lower floor". The first is decorated with stalactites, stalagmites and flowstones with typical dark brown colour, sometimes with a little reddish tinge. The "upper floor" consists mainly of coral forms.

2.1 Present Climate Conditions

The available data on the climate of Kilkis come from the Halkidona station 37 km to the south and

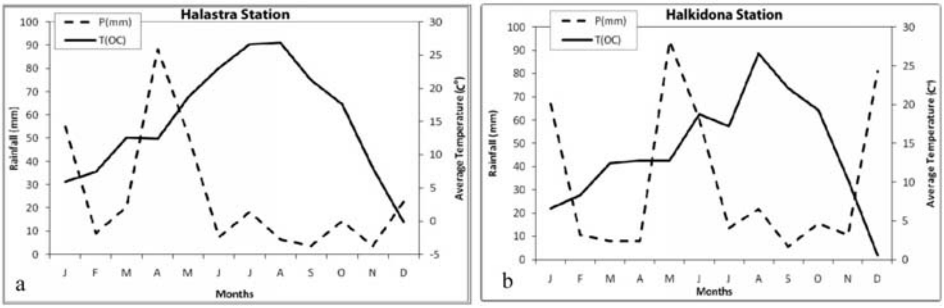

Fig. 2: Plot of average monthly rainfall (P) and temperature (T) from Halastra (a) and Halkidona (b) meteorological stations.

the Halastra station 26 km to the north of Agios Georgios cave. Average annual rainfall at these two sites is 343 mm and 454 mm, respectively. The average annual temperature at Halkidona is 16 °C and at Halastra is 15.5 °C (Fig. 2a, b). The hottest month is typically August, when mean monthly temperature is about 27 °C, while the coldest month is December when mean annual temperature approaches 0 °C. The local present-day climate at the Agios Georgios site is sub-humid Mediterranean, characterized by strong seasonal contrasts. The two instrumental records yielded a mean annual precipitation of 424 mm/year and a mean annual temperature of 15-17 °C for the period 1992–2006. Evaporation commonly exceeds precipitation from June to early September. The mean annual temperature in the cave is 16±1 °C and the humidity is about 95%.

3. Sampling and analytical methods

Sampling and study of the Agios Georgios speleothems were licensed to us by the Greek Ministry of Culture and Tourism, Ephoreia of Paleoanthropology and Speleology of Northern Greece (Licence No. ΥΠΠΟ/ΣΥΝΤ/Φ44/ 3898/88161). Three speleothems were sampled from different galleries of the the Agios Georgios cave. When cut vertically in sections parallel to the growth axis, they present well developed laminae zones. The AG1 sample is a stalactite (181mm long and 56mm wide, Fig. 3) which was chosen for further chemical analysis because it grew in a place without episodic flood. Twelve polished -thin sections were prepared along the stalagmite axis in order to observe the carbonate fabrics and the laminae under an optical microscope. Scanning electron microscope (SEM) equipped with EDS and WDS, at the Laboratory of Electron Microscopy and Microanalysis, University of Patras, was employed to examine crystal microstructure as well as to perform quantitative electron microanalyses. All elements were analyzed by an electron-dispersive X-rays (EDX) using EDS and WDS detectors attached to a JEOL JSM-6300 SEM. Operating conditions were accelerating voltage 15 kV and beam current 3.3 nA with 4 μm diameter beam. EDS and WDS spectrum information with the ZAF correction software information was used. The total counting time was 60 sec and dead-time 40 %. Synthetic oxides and natural minerals were utilized as standards for our analyses. Detection limits are ~0.1 % and accuracy better than 5 % was obtained.

4. Petrography of Speleothems

4.1 General

Each speleothem is consisted of multiple layers which have an annual or a subannual origin (Frisia et al., 2000). The layers may comprise either a single or various fabrics. Factors like chemistry and flow of par-

Fig. 3: AG1 stalactite cut vertically in section parallel to growth axis.

ent waters, the supply of ions to growth sites and the rate of CO_2 outgrassing are related to the crystal morphology of speleothems. Kendall and Brougthon (1978) pointed out that stalagmite are composite crystals from individual crystallites. The surface of crystals could be smooth or show steps and kinks, crystal defects stems from the incorporation of foreign ions, misfits at implying growth surfaces and condensation of vacancies (Wenk et al., 1983). Other misfits may originate from fluctuating flow rates, exposure of the growing crystal faces to the cave air, rapid outgrassing or dissolution (Fairchild et al., 2007).

4.2 Fabrics observed in the Agios Georgios speleothem

The collected sample cut along it axis show alternations of multicoloured laminae of variable thickness (Fig. 3). Notably, shows any asymmetric development with its axis to be shifted towards the stalactite periphery.

Columnar fabric consists of composite calcite crystals with length to width ratio ≤ 6:1 (Fig. 4a). Each composite crystal is made up of innumerable crystallites. The crystals have straight boundaries, uniform extinction and their long and optic axes oriented more or less normal to growth surfaces. In the studied samples crystallites are stacked in order, which is characteristic of columnar fabric, along with the lack of ring diffraction patterns in the composite crystals. The most common orientation of crystallite boundaries is parallel to the facet (1014) and crystallite habit is {1014} rhombohedron, and frequently the boundaries of crystallites are marked by micropores. The crystallites usually terminate with euhedral tips with flat faces (Fig. 4b). This fabric rarely shows competitive growth phenomena but the crystallites that form columnar fabrics are characterized by few dislocations, and it is probable that they grew through the spiral growth mechanism. At Agios Georgios stalactite columnar fabric forms translucent layers, which show annual lamination.

Another textural type observed in sample AG1 is *fibrous fabric*, which is characterized by calcite crystals with length to width ratio ≥ 6:1 and irregular crystal boundaries due to competitive growth phenomena (Fig. 4c, d, e). Competitive growth results in selective elimination of those crystals whose c-axes are not perpendicular to the substrate. Local Mg-bearing fibrous calcite crystals intergrow with pure calcite (Fig. 4f). In some cases, this type of fabric is characterized by the presence of patches of dolomite. Fibrous fabric layers are translucent and alike to columnar fabric.

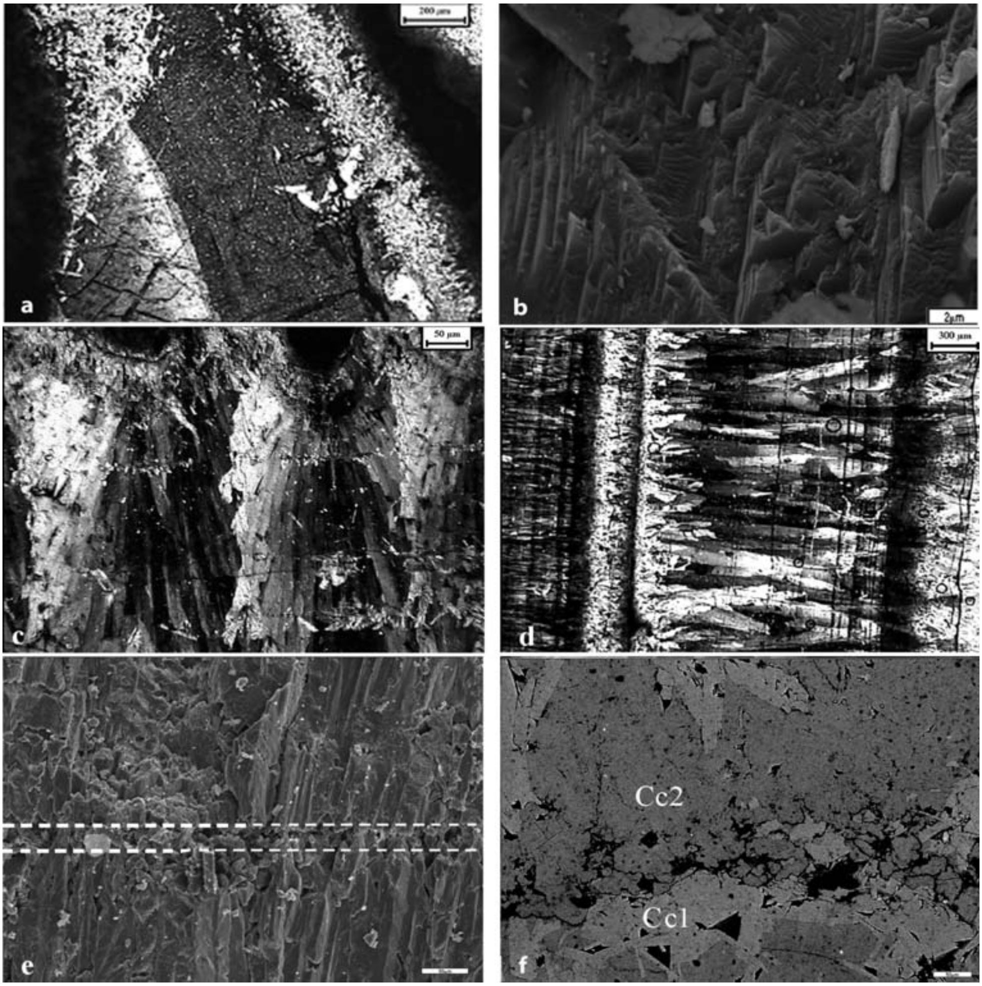

Fig. 4: Types of fabric and inclusion patterns from the stalactite of Agios Georgios Cave (a) Columnar Fabric photomicrograph, showing straight composite crystal boundaries and lack of visible laminae. The composite crystals have uniform extinction (Nicols +) (b) Secondary electron image showing trigonal crystallites with step surfaces. (c) Fibrous Fabric. Photomicrograph from AG1 shown competitive growth phenomena which result from those crystals whose c-axes are not perpendicular to the substrate. (d) Each layer of fibrous fabric is marked by microsparite (Nicols +) (e) Secondary electron image of two fibrous fabric calcite layers separated by thin layer of microsparite (f) Backscattered electron image of pure calcite (Cc1) interlayered with Mg- bearing calcite (Cc2); scale = 50μm.

Calcite with *microcrystaline fabric* in AG1 sample stalactite (Fig. 4g) form laminae layers with alternations between white and dark laminae and in places porous layers. Few crystallites grow in optical continuity with substrate, commonly in different orientations. This misorientation yields the serrated to interfingered boundaries typical of extinction, which may crosscut each other. Detrial muscovite grains up to 50μm and Fe-oxides exist in voids mainly in the dark laminae of microcrystalline calcite. In places halloysite and gibbsite occur, too; preliminary investigation of these clays suggested that they are resulted from microbial activity (Fig. 4h).

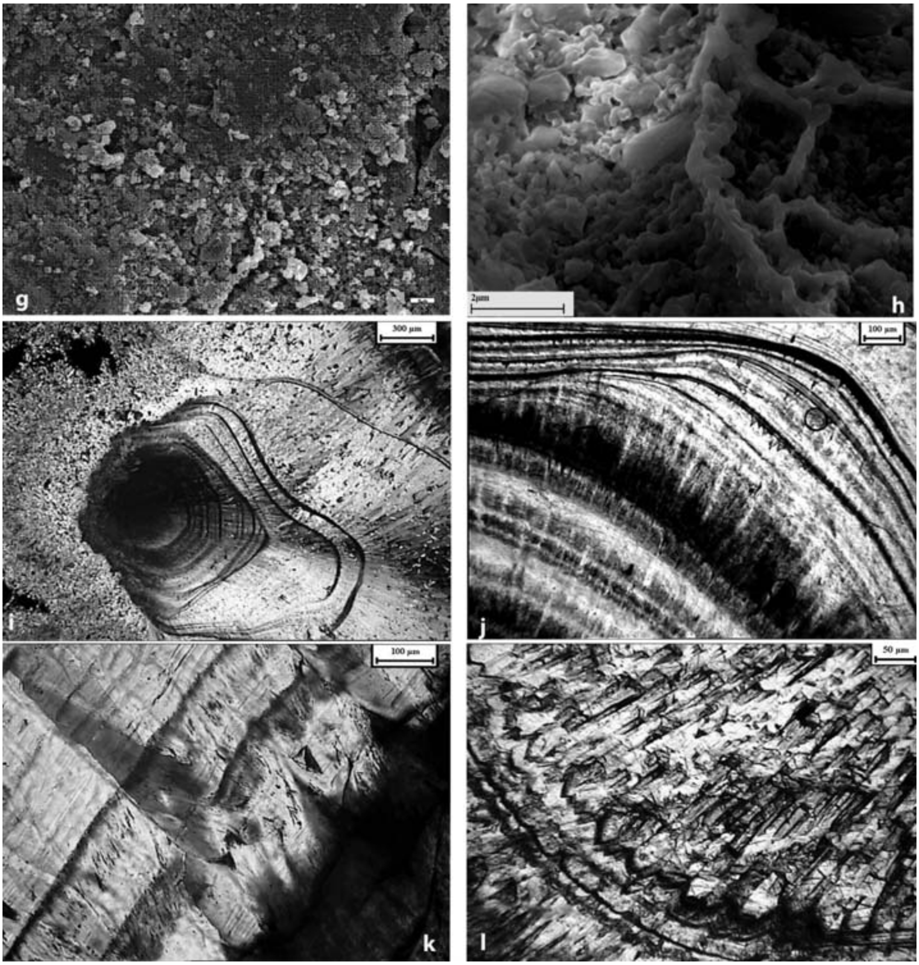

Fig. 4 (continued): Types of fabric and inclusion patterns from the stalactite of Agios Georgios Cave: (g) Secondary electron image showing crystallites exhibit rugged surfaces with macrosteps (scale = 5μm). (h) Secondary electron image of a void where microbial activity forms clay minerals. (scale = 2μm) (i) Bulbous mass of pseudopleochroic calcite. Type 1 growth layers contain large thorn like inclusions. Crossed polarized light (scale=300 μm). (j) Microcrystalline fabric. Photomicrograph showing dark drowns and white lamina. (k) Type 3 growth layers where former crystal terminations are defined by bands of pseudopleochroic calcite; crossed polarized light (scale = 300 μm). (l) Very well defined former crystals terminations by pseudopleochroic calcite; plane polarized light (scale = 50 μm).

4.3 Laminae Types

In thin sections cut normal to the stalactite long axis five type of growth layering were recognized. The layers of the first type are smooth curves with parallel to subparallel linear inclusions (*Type 1*). Another type of layers similar to *Type 1* (Fig. 4i) form smooth curves, which are defined by the concentration of inclusion. These inclusions are not visible with a light microscope so they impart pseudopleochroism to the calcite (*Type 2*, Fig. 4j). In *Type 3* layers are also defined by pseudo-pleochroic calcite but, instead of being smooth curves, they define former positions of rhombohedral (rarely scalenohedral) crystal faces (Fig. 4k). Such terminations may be complete or incomplete. In the latter case the growth layers combine the features of layer *Types 2* and *3*. Some inclusion-defined crystal terminations are not now associated with crystal boundaries. *Type 4* layers also define former calcite crystal faces like *Type 3* but are themselves defined by concentrations of linear inclusions (Fig. 4l). Layers characterized by the presence of impurities commonly separate layers with different crystal habit (*Type 5*).

5. Mineral Chemistry

Microanalytical work was carried out in carbonate crystals from each fabric of stalactite. The most common phase in all types of fabrics is pure calcite. In places with fibrous fabric, Mg-bearing calcite is also present with MgO ranging from 0.45 to 2.10 wt %; local dolomite patches were also analyzed (Fig. 4f). Representative results are given to Table 1.

Table 1. Representative chemical microanalysis of crystals from the AG1 stalactite sample.

Analysis No.	*AG1_1*	*AG1_2*	*AG1_3*	*AG1_4*	*AG1_5*
Mineral	***Calcite***	***Calcite***	***Mg-Calcite***	***Mg-Calcite***	***Dolomite***
FeO	-	-	-	-	0,68
MnO	-	-	-	-	-
MgO	0.06	0.14	2.10	1.58	19.95
CaO	55.85	55.83	53.87	53.7	32.93
Total	**55.91**	**55.97**	**55.87**	**55.28**	**53.56**
Stoichiometric formulae on the basis of 2 oxygens					
Fe^{2+}	-	-	-	-	0.017
Mn^{+}	-	-	-	-	0.000
Mg^{+}	0.003	0.007	0.103	0.079	0.907
Ca^{2+}	1.997	1.993	1.897	1.921	1.076

6. Discussion

Visible lamina thickness and repeated pattern of fabrics from AG1 stalactite reflect climate variations through the relationship between growth rate, climatic and geochemical parameters. Variations of seasonal alteration of fabric and/or mineralogical defining couplet and as, well as impurities during infiltration events have been shown generally to occur on an annual scale (Genty et al., 2001; Baker and Genty, 2003). In different environment settings depositions of different phases of $CaCO_3$ occur and as a result visible laminae could be interpretated as regular alteration of arrangement in space of crystals with the well defined morphology (texture or fabric, Onac, 1997; Frisia et al., 2000; Frisia et al., 2002). In sample AG1, connection between thickness of lamina and the environment variation could be achieved by the fact that in wet period and in high flow rates the thickness of layers increases. In contrary, at dry periods the thickness of visible layers decreases. If, during these periods, evaporation exceeds precipitation, which is related to the modern summer period in the area, then it is probable that this factor may additionally determinate the type of thin layers. Another connection between visible laminae and fabrics has occurred in this study. It is noticeable that during periods of infiltration (in seasonal high flow rates) the input of detrital and colloidal materials is more often (Borsato et al., 2007) and fibrous fabric is more likely to appear. In dry seasons where drip rate is slow lamina thickness is fine and columnar fabric is dominant. Also chemical variations in the water are reflected by chemical differences in the precipitated calcite, thus explaining the occurrence of both Mg-bearing and pure calcite crystals with microcrystalline fabric.

The calcite crystals of columnar fabric lack diffraction patterns and are crystals with low density defects. This is because the crystallites are stacked in order and all of them have the same orientation with respect to substrate (Kendall, 1993). The crystallite surfaces and sizes may vary, while the only crystal defects are few dislocations that grew with spiral mechanism. Spiral growth is more common at low supersaturation and can continue even if the fluid is close to saturation (Sunagawa, 1984). Therefore, it is considered as the dominant growth mechanism for columnar fabric crystallites (Frisia et al., 2002). The crystallites that formed in summer are characterized by evolution from smaller grains with rough surfaces to larger grains with flat faces; the winter crystallites are commonly characterized by rough surfaces. Columnar fabric forms in an environment of constant discharge, low and fairly constant degree of supersaturation and negligible impurity content. Accordingly, the layers with columnar fabric observed in the collected samples suggest formation under similar conditions.

Two factors are responsible for acceleration of fibrous fabric: 1) the larger number of crystallites due to more nuclei present and 2) faster growth rate induced by higher flow velocities (Frisia et al. 2000; Frisia et al., 2002). Both of these factors will result in faster achievement of parallel compromise boundaries and hence fibrous fabric. Fibrous fabric is generated only when flow rates accelerate crystal growth rate and increase heterogeneous nucleation, suggesting that the relevant layers in the Agios Georgios sample were formed under higher drip rates than those forming columnar fabrics.

Microcrystaline fabric usually forms under conditions of mean discharge, higher than those related to columnar fabric, low supersaturation and where the air flow is absent (Frisia et al., 2003). It is associated with insoluble residue like clay minerals (Huang et al., 2001). Clay minerals in AG1 sample can be found in void spaces, pores and bulbous masses which are compatible with their association to the microcrystalline texture (Fig. 4i). These microfabric evidences suggest that microorganisms have actively participated in the genesis of speleothem (Baskar et al., 2007). The formation of the clay minerals stems from the alteration of silicates and is probably related to microbe activity. The role of microbes is important because they act as nucleation sites to calcite precipitation and in many cases appear to control the types of crystals that form (Jones, 2001; Baskar et al., 2009). Different types of layering and inclusion patterns from AG1 stalactite steams from the perfect or less perfect coalescence between crystallites. If crystallites have the same orientation and identical lattice orientation with the substrate will combine to give a single crystal, and thus an inclusion-free calcite layer. Less perfect coalescence allowing the entrapment of impurities and will give rise to inclusion bearing layers (Kendall and Broughton, 1978). The variations in either the supply or the rates of absorption of impurities give rise to variations in impurity concentration which thus comes to define a growth layering.

All the above fabrics have been formed under isotopic equilibrium and stable isotopes (^{18}O and ^{14}C) suggested that fibrous calcite developed during cold environment episodes whereas microcrystalline and columnar fabrics have been crystallized under warm conditions (Antonelou, 2007).

7. Conclusions

Stalactite AG1 from Agios Georgios cave, Kilkis, N. Greece, is a calcite laminated stalactite with visible laminae, which are due to different chemical and environmental conditions. Three types of calcite fabrics have been detected. Columnar and microcrystalline fabrics formed during warm climate episodes while calcite crystals that show fibrous fabric have grown under conditions of rapid fluid discharge and low temperatures. The interpretation of fabrics can give as a clue about the paleoclimatic conditions during the formation of stalactite and alternations of warm and cold climatic episodes that influenced the area of N. Greece can be suggested.

8. References

Antonelou, A., 2007. *Study of speleothems from Agios Geogios Cave, Kilkis: Investigation of paleoclimatic environmental conditions using stable isotopes of C and O*, Master Thesis, University of Patras, 111-171pp.

Baker, A. and Genty, D., 2003. Comment on "A test of annual resolution in stalagmites using tree rings", *Quaternary Research* 59, 476-478.

Baker, A., Smith, L.C., Jex, C., Fairchild, I.J., Genty, D. and Fuller, L., 2008. Annually laminate speleothems : a review, *International Journal of Speleology* 37, 193-206.

Baskar, S., Baskar, R. and Kaushik, A., 2007. Evidences for microbial involvement in the genesis of speleothem carbonates, Borra Caves, Visakhapatnam, India, *Current Science* 92, 350-355.

Baskar, S., N., Baskar, R., Lee, N. and Theophilus, P.K., 2009. Speleothems from Mawsmai and Krem Phyllut caves, Meghalaya, India: some evidences on biogenic activities, *Environmental Geology* 57, 1169-1186.

Bertaux, J., Sondag, F., Santos, R., Soubiès, F., Causse, C., Plagnes, V., Le Cornec, F. and Seidel, A.,2002. Paleoclimatic record of speleothems in a tropical region: study of laminated sequences from a Holocene stalagmite in Central–West Brazil, *Quaternary International* 89, 3-16.

Borsato, A., Frisia, S., Fairchild, I.J., Somogyi, A. and Susini, J., 2007. Trace element distribution in annual stalagmite laminae mapped by micrometer-resolution X-ray fluorescence: Implications for incorporation of environmentally significant species, *Geochimica et Cosmochimica Acta* 71, 1494-1512.

Fairchild, I. J., Frisia, S., Borsato and A.Tooth, A. F., 2007. Speleothems. In Nash D. J. and McLaren S. J (Eds.) *Geochemical Sediments and Landscapes*, Oxford, Blackwell, 200–245pp.

Fairchild, I.J., Smith, C., Baker, A., Fuller, L., Spölt, C., Mattey, D., McDermott, F. and EIMF, 2006. Modification and preservation of environmental signals in speleothems, *Earth Science Reviews* 75, 105-133

Ford, D.C. and Williams, P.W., 1989. *Karst geomorphology and hydrology,* London, Unwin Hyman, 601pp.

Frisia, S., Borsato, A., Fairchild, I.J. and McDermott, F., 2000. Calcite fabrics, growth mechanisms, and environment of formation in speleothems from the Italian Alps and southwestern Ireland, *Journal of Sedimentary Research* 70, 1183-1196.

Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F. and Selmo, E.M., 2002. Aragonite-calcite relationships in speleothems (Grotte de Clamouse, France): environment, fabrics, and carbonate geochemistry, *Journal of Sedimentary Research* 72, 687-699.

Frisia, S., Borsato, A., Preto, N. and McDermott, F., 2003. Late Holocene annual growth in three Alpine stalagmites records the influence of solar activity and the North Atlantic Oscillation on winter climate, *Earth and Planetary Science Letters* 216, 411-424.

Genty, D., Baker, A. and Vokal, B., 2001.Intra- and inter-annual growth rate of modern stalagmites, *Chem-*

ical Geology 176, 191–212.

Genty, D.and Quinif, Y., 1996. Annually laminated sequences in the internal structure of some Belgian stalagmites-importance for paleoclimatology, *Journal of Sedimentary Research* 66, 275–288.

Huang, H. M., Fairchild, I. J., Borsato, A., Frisia, S., Cassidy, N. J., McDermott, F. and Hawkesworth, C. J., 2001. Seasonal variations in Sr, Mg and P in modern speleothems (Grotta di Ernesto, Italy), *Chemical Geology* 175, 429–448.

Jones B., 2001. Microbial Activity in Caves—A Geological Perspective, *Geomicrobiology Journal* 18, 345-357.

Kaufman, A., Wasserburg, G.J., Porcelli, D., Bar-Matthews, M., Ayalon, A. and Halicz, L., 1998. U–Th isotope systematics from the Soreq cave, Israel and climatic correlations, *Earth and Planetary Science Letters* 156, 141–155.

Kendall, A.C., 1993. Columnar calcite in speleothems – discussion, *Journal of Sedimentary Petrology* 63, 550-552.

Kendall, A.C. and Broughton, P.L., 1978. Origin of fabrics in speleothems composed of columnar calcite crystals, *Journal of Sedimentary Petrology* 48, 519–538.

Kockel, F. and Ioannides, K., 1979. *Geological map of Greece*, 1:50000 scale, Kilkis sheet. Institute of Geology and mineral exploration (IGME), Athens.

Onac, B.P., 1997. Crystallography of speleothems. In: Hill, C.A., Forti., P. (Eds.), *Cave Minerals of the World*, 2nd edition,. National Speleological Society, Alabama, Huntsville, 230-235pp.

Sunagawa, I., 1984. Growth of crystals in nature. In: *Materials and Science of the Earth's Interior* (Eds. Sunagawa, I.), Tokyo, Terra Scientific Publishing Company, 63–105 pp.

Wenk, H.R., Barber, D.J. and Reeder, R.J., 1983. Microstructures in carbonates. In: Reeder R.J. (Eds.), Carbonates: Mineralogy and Geochemistry, *Reviews in Mineralogy*, 11, Mineralogical Society of America, Washington D.C., 301- 367 pp.