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Decadal-scale Holocene climate variability from annually layered ice deposits in caves						

## Project Summary

### Intellectual Merit

The principal investigator requests funding to recover an ice core from Scarisoara Ice Cave in the northwestern Romania, and produce a high-resolution, multi-proxy late Holocene climate history for this data-sparse region of central-southeastern Europe. The principal investigator and his colleagues will examine the modern conditions and sensitivities of cave glaciers to climate-forcing factors and the range of climate-related parameters measured in the ice cores (e.g., stable isotopes, concentrations of chemical species, trace gases). The proposed site has weather stations already installed by the researchers. These stations measure a range of variables required to model the exchange of energy between the cave and the outside atmosphere and the ice mass balance at this specific site.

The length and resolution of our proposed ice cave record allows addressing the same kinds of questions that have been addressed by high-resolution polar ice core sequences. Indeed, one of the great strengths of the layered ice block is the capability to capture inter-annual to decadal climate signals based on stratigraphic variations in oxygen and hydrogen stable isotope content, chemical content, and trace gases. As the cave is located in mid-latitude, low elevation region, it holds promise for providing insight into different aspects of climate over southeastern Europe and in helping to reconstruct past environments using pollen assemblages, fossil leaves, and wood trapped within the ice. These approaches allow, in combination with other multi-proxy records outside the caves, correlation between geographically distant sites and may point out abrupt climate change events and their linkage to the North Atlantic Oscillation (NAO). The preliminary studies at the proposed site have produced promising results in relating the ice core signals to other late Holocene climatic and environmental events archived in peat bogs, tree ring, speleothems, and marine sediments. In addition to the proposed ice core data, we will produce complementary paleoenvironmental records from calcite speleothems collected from the same cave.

This project has five key scientific goals: (1) a physical understanding of atmosphere-ice cave deposition interactions; (2) validation of relationships between proxy data (e.g. isotope ratios or chemical concentrations) and the climate variables of interest (e.g., temperature, precipitation); (3) reconstruction of high-resolution records of temperature, precipitation, and atmospheric circulation patterns using isotopes of oxygen and deuterium, major ionic chemistry, and trace gases measurements; (4) integration of these records with other paleoclimatic proxy records from Romania and across Europe to reconstruct the late Holocene decadal to annual climate variability required to discern abrupt climate changes; and (5) development of an international network of cave ice core climate data to produce statistically meaningful reconstructions for the last two millennia.

#### Broader Impacts

The research will likely have broad impact on the wider science community by providing insight into how climate forcing mechanisms, interactions, and feedbacks are reflected in midlatitude, low elevation, cave ice-core records. The science resulting from this project will aid in the development and correlations of high-resolution (decadal to annual) records of regional climate in central and southeastern Europe and their linkage to the NAO.

The project will directly support the next generation of paleoclimate scientists by supporting several undergraduate and graduate students and post-doctoral scholars, emphasizing cross-training in data acquisition, data analysis, and modeling, and ensuring that science results are disseminated to the broader public through popular science articles and educational products for visitors to Apuseni National Park. This study establishes strong international links that will facilitate the dissemination of knowledge in this emerging field of inquiry.

#### **Background and Rationale**

Records of past climates are important to our understanding of modern climatic variability and future climatic change. Karst caves are unique repositories for various forms of paleoclimatic information (Lauritzen, 2003; Fairchild et al., 2006), as many caves are well protected from destructive processes acting on the surface. Because karst is regionally widespread, climatic data from caves can be used to test space and time dependent climate models. The powerful methods available for age-dating speleothems (e.g. Dorale et al., 2004), combined with their highly resolvable stratigraphy, make them valuable archives of terrestrial climate proxy data, and they have emerged as an important complement to deep-sea sediments, polar ice cores, and other proxy climate data (e.g. Richards and Dorale, 2003; McDermott et al., 2005). Climatic proxies in speleothems include oxygen and carbon isotopic compositions (e.g. Dorale el al., 1992; Gascovne, 1992; Lauritzen and Lundberg, 1999; McDermott et al., 2005), various types of recurrent laminae (e.g. Baker et al., 1993; Shopov et al., 1994; Genty and Quinif, 1996), and major, minor, and trace element compositions (e.g. Roberts et al., 1998; Finch et al., 2001; Li et al., 2005). Using these proxies, time-series reconstructions of regional climatic variations at key stages is possible. Our ability to recover records at high resolution depends fundamentally on our analytical capabilities (Fairchild et al., 2006).

A few select caves at high-latitude locations (e.g. Canada, Norway) and mid-latitude locations (*e.g.* throughout the European Alps, Carpathians, and in the Caucasus) contain thick perennial ice deposits (Yonge, 2004) that have recently gained recognition to be unique paleoclimatic archives (Racoviță, 1994; Racoviță and Onac, 2000; Luetscher, 2005). Emil Racoviță, an eminent Romanian biologist, was the first to note the scientific potential of the ice block in the Scarisoara Cave for climatic reconstruction (Racoviță, 1921). This novel paleoclimatic archive is the target of our proposal.

The fairly unusual condition of significant ice deposition in a cave environment immediately raises the question: (1) What is the mechanism of cave ice accumulation and what are the physical and chemical interactions between the atmosphere and cave ice deposition? Over the past several decades, our group has made substantial progress in understanding and answering portions of this fundamental question (Racovită, 1972; Racovită et al., 1987; Racovită and Onac, 2000). For example, we have observed a good correlation between climate and ice block dynamics in Scarisoara Cave over the last 40 years (Racovită, 1994). Given these observations a second question arises: (2) How well would the climatic events present in the cave ice cores relate temporally and spatially to climatic variations elsewhere in Europe and throughout the globe? Although annually-resolved records from the upper five meters of the Scarisoara ice block have allowed meaningful correlations to other climate proxies (Serban and Racovită, 1987; Racovită and Serban, 1990), deeper in the ice we have had limited success in our ability to temporally relate observations at different localities. The main difficulty thus far has been the limitation of available analytical capabilities that would allow the precise and accurate dating of the ice in these deeper portions. However, if advanced capabilities would allow us to successfully quantify time throughout the ice sequence, a third question would be: (3) How does the Holocene oxygen and hydrogen isotopic signal recovered from ice cores at highlatitude/altitude sites relate to corresponding history of oxygen and hydrogen of ice cores from caves at mid-latitudes? All questions are clearly fundamental to an understanding of ice cave formation and assessing the climatic signal archived within the ice layers. The last question is relevant to the issue of major climatic anomalies during the Holocene (e.g., Holocene Optimum,

Little Ice Age) and may point out abrupt climate change events and their linkage to the North Atlantic Oceanic (NAO) oscillations.

Located in Eastern Europe, our chosen ice cave fill an important geographic gap between the Alps and the Caucasus (Fig. 1). Comparison of our Romanian data with data from the Alps ice cores (which are situated closer to the ocean and thus record a stronger influence of the NAO) and that of the Caucasus (situated further inland), will enable a better understanding on how NAO extends its influence in the easternmost parts of Europe. Although a number of studies have revealed climate teleconnections between the northern high latitudes and the Middle East (Bar-Matthews et al., 1999; Fleitmann et al., 2003) and Far East (Wang et al., 2005), evidence from southeastern Europe is scarce (Onac et al., 2002; Feurdean and Bennike, 2004, Constantin et al., 2006).

We can, in principle, answer the above questions, and we can do so at high resolution and with precise time control, through the analysis of cave ice core sequences and well-chosen speleothems. Our proposed cave ice records occupy an important scientific niche because the length of the climate record obtained from mid-latitude, alpine glacier ice is limited to a few centuries. In contrast, ice core records from mid-latitude, low elevation caves such as we propose here, can extend beyond 4,000 years. The reminder of this proposal outlines how the highlighted questions will be addressed and the steps we will follow to achieve our proposal's goals.



Fig. 1. Location of cave site we propose to study (1). Also shown are other ice caves in Romania (2, 3), Slovakia (4), Austria (5, 7), Slovenia (6), and Switzerland (8), and the major alpine ice core sites. Main atmospheric influences over southeastern Europe are also indicated. See text for details.

#### **Research Plan Summary**

Over the past decade, Onac's research group and collaborators have laid the groundwork for answering the fundamental questions posed above. We now focus on recovering an ice core from the major ice cave in the Western Carpathians (Transylvania, Romania; Fig. 1) from which we propose to obtain high resolution, <sup>14</sup>C-dated time series of ice  $\delta D$  and  $\delta^{18}O$ . The ice isotopic time series will be compared to the  $\delta^{18}O$  time series of U-Th dated calcite speleothems collected from the same cave as the ice core. Specifically, we propose to produce a high-resolution cave ice  $\delta D$  and  $\delta^{18}O$  time series, and two speleothem  $\delta^{18}O$  time series covering the last ~5,000 years. As this proposal extends previous and ongoing research projects, we have already published or are in the final stages of publishing glaciological data on Romanian ice caves, and preliminary speleothem climate records that encompass the time span between the last interglacial and present (Racoviță and Onac, 2000; Onac, 2001; Cittterio et al., 2005; Holmlund et al., 2005; Persoiu, 2005; Zak et al., *in review*).

To ensure the success of this proposal our research strategy takes into consideration the following items: the research team, samples, analytical means, and adequate funding. These issues are addressed below.

<u>Research team</u>. The principal investigator, Dr. Bogdan Onac, is originally from Romania and is now an Assistant Professor at the University of South Florida (USF). Before he joined the Department of Geology at USF he worked for 15 years at the Speleological Institute of the Romanian Academy of Sciences. Over the last five years, Onac was the head of the institute and established a network of collaborators comprised of prominent glaciologists and karst scientists with whom he started various paleoclimatic research programs. The PI is a member of the Scientific Board of Apuseni Natural Park where all target caves are located. This connection will help in obtaining permission for coring and sampling and will also help in gaining access to climatic data from meteorological stations within the park.

Dr. Jeff Dorale (co-PI), Assistant Professor at the University of Iowa, brings to the table expertise in paleoclimatic reconstruction using speleothems. Dorale will oversee the generation and interpretation of the stable isotope and U-series data of the collected speleothems. For this project, the U-Th dating of speleothem sub-samples will be done at Taiwan National University in collaboration with Dr. Chaun-Chou Shen. Co-PI Dorale and Dr. Shen are associates from shared post-doctoral research experience at the University of Minnesota Radiogenic Isotope Lab, under the advisorship of Dr. R.L. Edwards. Prof. T. Stocker (University of Bern, Switzerland) is a world-leading expert on Polar ice cores analyses and climate modeling. Prof. P. Holmlund's (University of Stockholm, Sweden) expertise in alpine glaciology will help with the glaciological aspects of the ice cores. Drs. K. Zak and A.V. Bojar from the Institute of Geology (Czech Academy of Sciences) and University of Graz (Austria), respectively are specialists in stable isotope investigations of cryogenic carbonates. Two of the PI's former colleagues at the Speleological Institute, Drs. T. Tamas and S. Constantin have experience in cave paleoclimate (their doctoral works were on this topic) and karst areas of Romania. A. Persoiu and Z. Kern are PhD students at University of South Florida and Budapest University in Hungary.

<u>Samples</u>. The cave targeted for this project is easy to access and sample. Our preliminary work showed that ice cores could be drilled without problems at any of the Romanian sites. <sup>14</sup>C dating of organic material from the Focul Viu ice core indicates an age of 1,711 years BP at a depth of 6.8 m (out of ~24 m). Ages around up to 3,780 cal. years BP were obtained on pine

needles and branches from Scarisoara at depths up to 15 m (total thickness of the ice block is  $\sim$ 25 m). Therefore, we can safely assume that the ice core samples will cover the time range of interest. Calcite speleothems are available in rooms that surround the ice block. Our earlier work on 15 samples from Scarisoara (Onac, 2001) has identified several late Holocene speleothems. Thus, we have access to a number of samples with appropriate preliminary analyses and, furthermore, if additional samples are needed for cross-examinations or replication tests, Scarisoara Cave can provide the necessary materials (ice or speleothems). Analytical Facilities. The oxygen and hydrogen stable isotope analyses on speleothems will be performed at the College of Marine Sciences, St. Petersburg campus of the University of South Florida. If additional facilities are needed to handle our required throughput, we have access to two well-know stable isotope laboratories at the University of Bern (Switzerland) and University of Idaho (Moscow, ID). The first one will also perform the trace gases analyses in the ice. The <sup>230</sup>Th dating of speleothem sub-samples will be done at Taiwan National University using a Thermo Electron Element II ICP-MS in collaboration with Dr. Shen. The <sup>14</sup>C ages will be obtained at the Gliwice Radiocarbon Laboratory in Poland. This project requires large numbers (~5,000) of oxygen and hydrogen measurements (from ice, precipitation, and cave drip waters).

<u>Money</u>. Here we request the bulk of the funding to support drilling of an ice core, stable isotope analyses, scientific interpretation and publication of high-resolution Late Holocene paleoclimatic data. We have made every effort to reduce this request to NSF by securing other sources of funding for portions of this project. We have secured four independent funding from the Ministry of Education and Research in Romania to cover parts of the first and second year field work, travel and accommodation within Romania, and half of the costs of the stable isotope measurements of speleothems (see Onac, Constantin, and Persoiu, Current & Pending Support). Dr. Shen has graciously agreed to provide all the required U-Th analyses at no cost to the project, in exchange for participating in the publication of results using these analyses (see letter of support at end of document).

We propose the following itinerary for our research strategy over the next three years (see the included Gantt diagram).

- (1) We will establish a present-day calibration for our chosen climatic proxies. We have already taken steps in this direction by setting up automatic weather stations (temperature, humidity and rain gauge) outside and inside the cave. To capture the seasonal isotopic signal we will collect monthly water samples and meteorological data throughout the first two years. We also plan to install drip loggers and water collectors inside the cave at two different locations. These loggers are available to the PI;
- (2) All collected water samples will be measured for oxygen and hydrogen isotopic composition just before the grant ends;
- (3) Drill and obtain an ice core (~25 m) from Scarisoara ice cave. The ice core will be photographed and visually examined in the cave and then transported in insulated boxes cooled with dry ice and stored at -30 °C in cold rooms;
- (4) Obtain detailed description and electrical conductivity measurements along the ice core;
- (5) Perform a count of ice layers on the vertical ablation wall and in the ice core. Cross-correlation of the two counting processes and computing ice growth age model based on incremental (laminae), <sup>14</sup>C, and <sup>210</sup>Pb dating results;

- (6) Extraction of samples for stable isotope (collected every 1 cm along the ice core), trace gases analyses (collected every 1 cm from the upper 5 m of the ice core), and <sup>14</sup>C dating (from core and exposed ice wall in cave). This step will be performed either directly in the cave or in the cold room;
- (7) Oxygen and hydrogen stable isotope measurements and trace gases determinations on ~5,500 ice samples;
- (8) A candlestick calcite speleothem will be collected, cast in epoxy for protection and cut in two halves along the growth axis. Only speleothem samples that show a well preserved laminated structure and that cover the last ~5,000 years will be selected for detailed crystal fabric, stable isotope, and U-Th dating. We use one half for sub-sampling; both for high-resolution oxygen and carbon stable isotopic measurements, with millings taken along the central axis of the stalagmite, and for U-Th dating, with millings taken just off-axis. The other half of the stalagmite will be reserved for non-destructive techniques. We plan to perform lamina counting on speleothem slabs. This will be done to refine the age model based on U-Th data and to compare with the incremental dating of ice. In addition, microscopic studies (standard polarized and epifluorescence) will examine the calcite crystal fabrics, which are crucial to understand drip rate, growth intervals, and other variables of interest.
- (9) Finally, the ice core data will be interpreted and compared to those retrieved from the speleothems. For a more accurate picture of the changing climate and environment over the past 4,000 years, and to confirm our findings, our data will be compared to other records (pollen, polar and alpine ice cores, deep-sea sediments, etc.). Results of this study will be published in peer-review journals and presented at national and international meetings. Our data set will be available from the World Data Center (ice cores/speleothems), Boulder, CO.

# Gantt Diagram of our Research Strategy

2007	07 2008								2009												20	010		Years/Objectives		
																										Install drip loggers & water collectors
																										GPR imaging of the ice block
																										Ice core drilling in SCS
																										Ice blocks stratigraphy in SCS
																										Collect & cut speleothem
																										Ice core visual stratigraphy & description
																										ECM & ice layer counting
																										$^{3}$ H, $^{137}$ Cs, $^{210}$ Pb dating of ice
																										<sup>14</sup> C dating of organics in ice
																										Ice: Sampling/analyses of $\delta^{18}$ O & $\delta$ D
																										Ice: Sampling/analyses of major-ions
																										Speleothems: microscope studies
																										U/Th TIMS dating of speleothems
																										$\delta^{18}$ O, $\delta^{13}$ C in SCS speleothems
																										Water analysis ( $\delta^{18}$ O, $\delta$ D)
																										Data synthesis & comparisons
																										Publication of results
																										PhD work

SCS: Scarisoara Cave; GPR: ground penetration radar; ECM: electric conductivity measurements.

#### **Climate records in ice cores**

<u>Caves as cryogenic environments</u> The presence of massive ice in caves at high latitude or altitude is expected due to mean annual temperatures below 0 °C (Yonge, 2004). However, less common are the perennial ice accumulations found in caves at lower elevations in mid-latitude regions where the mean annual temperature is above 0 °C. Here, the presence of ice is restricted to vertical or steeply downward sloping caves with only one entrance, and in which



a particular aerodynamic exchange occur. During winter, the cold, dense air sinks and replaces the warmer air fraction from the upper part of the cave (Fig. 2). In summer, the cold air circulation breaks into a convection cell that is limited to the lower part of the cave (Fig. 2). The cold air remains trapped causing cooling of the bedrock and eventually leading to a unique glacial-type climate inside the cave (Bögli, 1980; Racoviță and Onac, 2000; Luetscher, 2005).

Such caves are especially interesting for ice core studies because they can lie at relatively low altitudes where alpine glaciers are not available. Moreover, these ice core climate proxy records can be calibrated against carbonate speleothem records collected from the very same caves.

#### Fig. 2. Schematic behavior of a cold air trap.

Generally, the cave temperature approximates the mean annual surface temperature (Wigley and Brown, 1976; Onac, 2000), so that at mid-latitudes the usual values are between 4 and 10 °C, whereas if glacial conditions are established in the cave environment, these values may be in the range of -5 to +1 °C. Therefore, in investigating the isotopic signal preserved in speleothems from the ice cave, the onset of ice accumulation should show a clear shift on the isotopic profile recorded in the stalagmite.

Once the thermal anomaly and glacial climate becomes established in the cave, ice begins to accumulate. Among many subsurface ice outcrops described throughout the world (Ford and Williams, 1989), the most common ones in the temperate climate belt are those derived from 1) snow accumulation and 2) congelation of percolating water. The shape of some cave entrances allows snow to be captured during the winter months. As time passes, snow transforms in firn, which through densification and recrystallization tends to form perennial, layered deposits conforming to floor topography. Percolation water and melting of snow at the bottom of shafts are the sources of water that build up major accumulations of congelation ice. Both types of ice deposits usually display clear, transparent to translucent layers separated from each other by darker, impurity-rich (soil particles, organic material, dust, cryogenic calcite) laminae (Fig. 3). Careful examination of these alternations can reveal the annual signal. This was demonstrated by lamina counting in the upper part of some ice blocks in which historical reference horizons exist (Racoviță and Onac, 2000; Luetscher, 2005). Annual cyclicity in the internal structure of these ice blocks is explained by summer



incorporation of impurities on the bottom of ponded water (at the ice block surface) that freezes in winter from the top downward.



<u>Ice caves in Romania and Europe</u>. Early observations on ice caves were reported in the form of short descriptions within general topic books (Trombe, 1952; Bögli, 1980). Only during the  $21^{st}$  century, some of the documented ice caves became the object of larger studies, mainly concerning ice morphology and dynamics. Although five ice caves are known in the Bihor Mountains (western Romania, Fig. 1), only two of them host ice deposits that exceed 20,000 m<sup>3</sup>, and it is one of these caves that has been selected for the present project. The average modern-day annual precipitation ranges from 1,000 to 1,200 mm, whereas the mean annual temperature at this sites is in the range of 4 to 6 °C. Within the Romanian ice caves, Racoviță (1984) distinguished three climatic zones: a glacial zone comprising the ice block, a periglacial section surrounding the ice block, and warm climate zones in the non-glaciated parts of the cave (Fig. 4).



Fig. 4. Cross-sections of two ice caves showing the climatic zones and the location of the ice blocks.

*Scărişoara Ice Cave* hosts an ice deposit with an estimated volume of  $\sim 100,000 \text{ m}^3$ . The entrance shaft of the cave (60 m in diameter and 48 m in depth) is located on the edge of the Scărișoara Plateau at 1,165 m asl. The total length of cave passages is 800 m.

The ice block, with a horizontal surface of about 3,200 m<sup>2</sup> is located in the Great Hall, from where it extends into three lateral rooms: The Church, Little and Great Reserve (Fig. 4a). The stratified ice block has a total thickness of 24.7 m. Based on pollen analysis, Pop and Ciobanu (1950), estimated the age of the lowermost ice layers as 3,000 years BP. Ice stalagmites occur in the vicinity of the ice block. The cave also contains a variety of calcite speleothems, which mostly occur in the inner, non-glaciated parts of the cave. *Focul Viu* (back-up cave) is a downward sloping cave (107 m in length), located at an altitude of ~1165 m, on the western margin of the Padiş karst plateau, in the central part of the Bihor Mountains. A small inclined shaft provides access to a large chamber ("Big Hall", 68x46 m), followed by a smaller one ("Small Hall", 20x5 m). A massif ice block (~35,000 m<sup>3</sup>) formed by diagenesis of snow and freezing of percolating water fully occupies the floor of the Big Hall (Fig. 4b). The ceiling of this room opens to the sky through a second, larger shaft. Large snow cones accumulate below both shafts. Between the northern side of the ice block and the host rock, a narrow opening (Rimaye) gives access to a lower, ice-free sector of the cave, delimitated by a vertical ice wall in which the ice stratification is visible.

Two major ice caves are known in the Austrian Alps (Eisriesenwelt and Rieseneishöhle), both located over 1,500 m asl (Fig. 1). Although extensive glaciological observations were carried out in the first half of the 20<sup>th</sup> century (Kyrle, 1923; Angermayer et al., 1926), no paleoclimate studies have been conducted in these caves in recent decades.

The world's largest ice block  $(110,100 \text{ m}^3)$  lies in Dobsinska Ice Cave, Slovakia (Fig. 1). The surface of the ice block is ~9500 m<sup>2</sup> and its maximum thickness reaches 26.5 m (Lalkovic, 1995). Smaller deposits of ice are documented from caves in Switzerland and Slovenia (Fig. 1).

The characteristic feature of the ice deposits in the Austrian, Slovakian, and Slovenian caves is that ice blocks accumulated on uneven floors and hence the ice layers are not horizontal like in the two Romanian caves. In addition, the ice within these former caves experienced repeated melting and freezing events causing cross-stratification in the ice block to occur. Therefore, the ice block stratigraphy is somehow compromised with the exception of some short sequences (in the uppermost part). *These characteristics form another major consideration in the selection of the ice cave from Romania for the present project.* 

#### Methods and preliminary results in dating the ice deposits in caves

Before radiometric dating came into use, attempts were made to establish the age of ice in caves using pollen assemblages. The first such investigation was undertaken by Pop and Ciobanu (1950) in Scarisoara Cave. They analyzed pollen grains from an ice sample collected at a depth of 12 m and gave an estimated age of ~3,000 years BP Later, similar investigations in ice caves from Austria indicated most ice deposits at these sites formed during postglacial or even historic time (Kral, 1968; Achleitner, 1995).

<u>*Radiometric methods.*</u> Invariably, the entrance in the ice caves is either a large, deep vertical shaft or a steep downward sloping passage. Both morphologies account for large quantities of organic material (leaves, branches, tree trunks, pollen) that fall and become trapped within the ice layers (Fig. 3). This represents an advantage over the classic polar and alpine ice cores because direct <sup>14</sup>C dating enables reliable chronologies to be established (Racoviță and Onac,

2000; Onac et al., *in prep.*). We have already dated by means of AMS <sup>14</sup>C, branches, leaves, and pine needles contained in cave ice of Scarisoara and Focul Viu caves. Fourteen radiocarbon ages (7 in each cave) provided us with ages between 325 and 3,780 cal. years BP, but none of the sample were collected from a depth greater than 15.2 m (Citterio et al., 2005; Holmlund et al., 2005; Onac et al., *in prep.*). This confirms our hypothesis that at the bottom of the ice block (~ 25 m) the age should be well over 4,000 years. Spötl and Mais (1999) and Lutscher (2005) reported radiocarbon ages no older than 1,500 years BP from caves in Austria and Switzerland. *These results were also taken into consideration in selecting the Romanian ice cave for this project.* 

In addition, dating of cryogenic calcite precipitated by freezing of bicarbonate-rich groundwaters in glacial-type cave environments is a promising alternative when organic matter is missing. Recently, one of our collaborators demonstrated that cryogenic calcite extracted from ice could successfully be dated by U-series methods (Zak et al., 2004).

For the younger most part of the ice blocks (i.e., the last 150 years), clear massive ice samples can be dated using short-lived isotopes such <sup>210</sup>Pb and <sup>137</sup>Cs (Gäggeler, 1995; Luetscher, 2005). Another reliable tracer for dating recent, specific (thermonuclear bomb tests), events is tritium (<sup>3</sup>H), which enters the cave via precipitation. The 1963 peak observed in precipitation was also detected in Monlesi (Switzerland) and Bortig Ice Cave (Romania) caves by Luetscher (2005) and Kern et al. (2006), respectively. Such stratigraphic markers in Focul Viu Cave enabled calculation of the ice accumulation rate (Forisz et al., 2004). *Incremental dating*. In both Scarisoara and Focul Viu the ice blocks have at least one exposed side (Fig. 4), hence direct counting of ice layers is possible. Based on changes in the visual properties of the ice (darker vs lighter seasonal increments) similar analyses will be conducted on the ice core. Once a record of incremental layers has been established, each layer of ice can be assigned an age in *ice-accumulation years* (number of annual layers below present surface). The preliminary results are encouraging. We performed laminae counting for the upper most 5 m of the ice block in Scarisoara Cave and we found 313 annual couplets of ice. Just below the last counted ice layer we radiocarbon dated a wood piece to 325±30 cal. years BP.

#### Oxygen isotope chronostratigraphy in ice cores.

<u>Background</u> The ratios of naturally occurring oxygen isotopes in precipitation samples can provide significant information relative to temperature, distance from source water, and evaporation. During evaporation from the ocean surface, atmospheric water becomes depleted in the heavier <sup>18</sup>O isotope by ~10‰. However, there is seasonal variability in this value, so that the range of  $\delta^{18}$ O between summer and winter precipitation over the ice sheets is commonly about 15‰ (Lowe and Walker, 1997). Hydrogen isotopes behave in much the same way as oxygen isotopes, a fact that was confirmed when comparing the deuterium profile from Vostok record with the oxygen isotope record in GRIP Summit core (Jouzel et al., 1990). Thus seasonal changes can be detected for the time period spanned by the ice core record by precise measurements of oxygen and hydrogen isotope variations.

Much of the information about past climate and environmental conditions on timescales from decades to hundreds of millennia, and the most direct and highest temporal resolution record of past atmospheric and precipitation chemistry come from polar and alpine ice cores (Petit et al., 1999; NGRIP, 2004; EPICA, 2004; Brook and Wolff, 2006, Thompson, 2004; Thompson et al., 2006). Cores drilled through several parts of the Greenland ice cap covering the Holocene, show that climate, albeit more stable than glacial time, still shows

significant variability (Dansgaard et al., 1993; deMenocal et al., 2000; Witt and Schumann, 2005). Abrupt shifts in climate (e.g., 8.2 ka cold event) have been reported from high- through low-latitude sites around the world, in a variety of archives when investigated with sufficient resolution (Alley et al., 1997; von Grafenstein et al., 1998; McDermott et al., 2001; Veski et al., 2004).

In addition to the polar ice work, research on several ice cores from temperate regions has proved the suitability of these records for both paleoclimatic and past atmospheric and precipitation chemistry studies (Cecil et al., 2004). In Europe, three high altitude regions were target for such studies (Scandinavia, the Alps, and the Caucasus), with most of the work carried out in the Western Alps (Monte Rosa, Mont Blanc, and Fieschernhorn (Schwichowski, 2004).

European climate is mainly influenced by the variations of the North Atlantic Oscillations (NOA) (and subsequently the strength of westerlies). Studies from both Western and Eastern European sites (Popovnin, 1999) revealed the presence of a climatic signal in the ice core records generated by the westerlies (Thompson, 2004). With this perspective, we believe high-resolution records of oxygen and hydrogen isotopes from our targeted ice caves would provide mid-latitude, low elevation counterparts to the high-latitude/altitude ice core records.

<u>Preliminary work</u> To date, limited attempts have been made to test the potential of perennial cave ice in isotope paleoclimatology (Serban et al., 1967; Marshall and Brown, 1974; MacDonald, 1994; Yonge and MacDonald, 1999; Luetscher, 2005). Nevertheless, oxygen and hydrogen isotopes have been analyzed on some short cave ice sequences. Serban et al. (1967) observed variations of the isotopic composition ( $\delta^{18}$ O and  $\delta$ D) of various layers in Scarisoara Cave and concluded that a periodicity can be observed. In a later study, Serban and Racoviță (1987) attempted to correlate isotopic information and particular stratigraphic elements (impurity-rich ice layers) with climate oscillations from other proxies. In this way, three major impurity layers in the upper part of the block were attributed to well-known warm intervals within late Holocene.



Preliminary oxygen isotope analyses were performed on three short sets of ice from Scarisoara Cave (44 samples from 0.05 to 0.5 m below the ice surface, 23 from 11 to 11.25 m, and 25 from 21.9 to 22.15) to assess whether seasonal patters are visible at different depths in the ice. Results show values of  $\delta^{18}$ O varying between -9 and -13‰ (Fig. 5). The values are consistent with regional isotope precipitation data provided for the last 10 years by the Romanian National Meteorological Institute.

Fig. 5.  $\delta^{l8}O$  values in three short ice profiles from Scarisoara Cave.

The oscillating signal is interpreted as a seasonal signature of the cave air dynamics. This interpretation concurs with similar observations made in the Canadian Rockies (Yonge and MacDonald, 1999) and in the Swiss Jura (Luetscher, 2005). The hypothesis is that low  $\delta^{18}$ O values correspond preferentially to early annual ice accumulations, which occur more readily during late spring when more percolating water becomes available and the cave behaves as cold thermal trap. Data from Scarisoara Cave suggests that the thickness of annual layers ranges from 3 to 9 cm, which corresponds to estimations provided by lamina counting on the upper part of the ice block. Therefore, *annual and intra-annual resolution* can be recovered.

A thorough paleoclimatic study requires a large number of oxygen and hydrogen isotope measurements. Considering the thickness of the ice block and the sampling protocol (every cm along the ice core), about 5,500 samples will be recovered. The majority of these analyses will be performed using the requested NSF funds.

#### **Speleothem climate records**

Speleothems have great potential for contributing to the field of paleoclimatology because they can exhibit a suite of favorable characteristics found in few other single archives. These characteristics include (1) the ability to date small carbonate sub-samples precisely and accurately by <sup>230</sup>Th methods (only rivaled by records that have truly annual layers), (2) high resolution (approaching that in ice core records), (3) continuous deposition over many thousands of years, and (4) the mechanisms of speleothem growth are sensitive to a number of climate variables (e.g., amount and composition of meteoric precipitation).

**High resolution U-series dating** The precision with which <sup>230</sup>Th ages can be determined by mass spectrometry as a function of sample size, uranium concentration, and age were outlined by Edwards et al. (1987) and have been recently reviewed by Dorale et al. (2004). In speleothem and other inorganic calcite work, both sample size and precision are related to error in age. Growth rates are often low, so that large sub-samples will integrate large time intervals and introduce error in age (if uranium concentrations and growth rates are not constant in this interval). On the other hand, large sub-samples contain more <sup>230</sup>Th atoms and therefore result in higher precision <sup>230</sup>Th ages. Thus, there is a tradeoff between spatial resolution in sub-sampling (for which small sub-samples are ideal) and precision in <sup>230</sup>Th age (for which large samples are ideal). In practice, using modern ICP-MS techniques (see Shen et al., 2002; Dorale et al., 2004), we can obtain the following results routinely with clean sub-samples of 50-100 mg and uranium concentrations of about 1 ppm (2 $\sigma$  errors): 300 ± 5 y, 1,000 ± 10 y, 5,000 ± 20 y, and 10,000 ± 40 y. In most cases except for very young sub-samples, the temporal error due to sampling resolution is small compared to the analytical error in <sup>230</sup>Th age.

<u>Preliminary results</u>. As part of a project aiming to identified speleothem growth intervals in Romania, 15 samples out of nine speleothems (flowstones and stalagmites) from Scarisoara Cave were dated by  $\alpha$ -counting U-series method. Three speleothems were found to be Holocene, but no further work was yet performed on any of them. In the proposed project, one of these stalagmites will be dated at high resolution using mass spectrometric techniques. **Oxygen isotopes in speleothems as measure of paleoclimate**. Oxygen isotopic variations in speleothems deposited under isotopic equilibrium conditions are potentially powerful tracers of climatic changes. Proper interpretation of  $\delta^{18}$ O variations in speleothems must consider (1)

the relationship of precipitation  $\delta^{18}$ O to the meteorological cycle, (2) oxygen isotopic fractionation during calcite deposition, and (3) the changing isotopic composition and temperature of the oceanic source. To test the fidelity with which the  $\delta^{18}$ O values of speleothem calcite reflect the combination of the oxygen isotopic composition of precipitation and temperature, the Replication Test was proposed by Dorale et al. (1998, 2002). The idea is that if different speleothems from the same cave record nearly identical isotopic compositions through time, then kinetic/vadose alteration processes are not significant, and the record can be interpreted as a primary environmental record.

In order to obtain a late Holocene record we collected a 35 cm long growing stalagmite (SCS) from the upper part of the Little Reserve (Fig. 4a). Cut lengthwise the speleothem shows alternating white-opaque and brown-translucent laminae. It also shows several minor



shifts in the growth axis but no signs of hiatuses. The base of the stalagmite was U/Th dated by of MC-ICP MS and yielded an age of  $2,577 \pm 357$  years BP.

Fig. 6.  $\delta^{18}O$  profile along the growth axes of SCS stalagmite.

Samples for stable isotopes (0.05 g) were taken at 1 mm intervals along stalagmite's growth axis. The oxygen profile shows drops of 0.8-1.5 ‰ in at least 4 periods over the last 2500 years (Fig. 6). We interpreted these as cold events based on the positive relationship found between meteoric water  $\delta^{18}$ O and temperature (Onac et al., 2002). It seems plausible that these distinct  $\delta^{18}$ O oscillations may be recording a pattern of decadal-scale climatic variability related to strength of the paleo-NAO. We can test this hypothesis with additional work involving other speleothems and rigorous U/Th dating, and comparison to our proposed ice core data. Recently, paleoclimate records emerged from several precisely dated Holocene speleothems from western Romania (Constantin et al., 2001, 2006; Onac et al., 2002; Tamas et al., 2005). These records will be compared to our data.

#### **Explicit comments regarding Broader Impacts**

Here we briefly highlight some of the Broader Impacts of our proposed research. Because the majority of the world's population live at mid- and low-latitudes, it is vital to understand how the environment is changing, on local, regional and global scales. Mid- and low-latitude glaciers and ice caves provide unique opportunity to look at how environment has changed in the past, how it is changing today, and to project possible changes in the future. To the people who live in these locations, understanding the short-term (centennial to decadal) atmospheric dynamics that control seasonal shifts as well as precipitation events is of paramount concern. Thus, such a research is important for our society. This proposal is intended to be a seed-project, which along with the other work in progress by the PI (see Current & Pending Support) will generate a more detailed knowledge of the nature, timing, and local/regional extent of climatic and environmental changes over the last 5,000 years and possible links to the NAO. Our work will establish climate records that can be used by the HOLIVAR (Holocene Climate Variability; ESF) and INTIMATE (INTegration of Ice-core, Marine And TerrEstrial; INQUA) programs, and possibly linked to the IPICS 2k array (International Partnership in Ice Core Science) project (Brook and Wolff, 2006). With the goal to provide full access to our results, all obtained data will be archived at the World Data Center, Boulder, CO.

This study establishes strong international links that will facilitate the dissemination of knowledge in this emerging field of inquiry. The fact that our collaborators include prominent glaciologists and paleoclimatologists (T. Stocker, University of Bern; P. Holmlund, University of Stockholm; K. Zak, Czech Academy of Sciences; A.V. Bojar, University of Graz) provides our team with direct connection to the international polar and alpine ice core science community. Our work will help in further educating two individuals in the Romanian scientific community on climate change issues. In this regard, they already published in peer review journals (Tamas et al., 2005; Constantin et al., 2006) and are willing to include paleoclimatology in their curricula. In addition, our project will partly support the ongoing doctoral research of A. Persoiu and involves the training of two other graduate student (Romanian and Hungarian) and three scientists internationally. Thus, the project will directly support the next generation of paleoclimate scientists, emphasizing cross training in data acquisition, data analysis, and modeling. At the same time we will ensure that the science results are disseminated to the broader public through popular science articles and educational products for visitors to Apuseni National Park.

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ORGANIZATION			POSAL	NO.	DURATIC			
UNIVERSITY OF SOUTH FIOLIDA				_	Proposed	Granted		
PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR		A	MARD N	0.				
DUYUAII F UIIAC		_NSF Fund	ed	FI	unds	Funds		
(List each separately with title, A.7, show number in brackets)	CAL		nths CLIMP	Reque	ested By	granted by NSF		
1 Pondan B Onag Assistant Professor			1.00	¢	5 000	¢		
2	0.00	0.00	1.00	φ	5,009	φ		
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6. ( 1) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)	0.00	0.00	0.00		0			
7 (1) TOTAL SENIOR PERSONNEL (1 - 6)	0.00	0.00	1.00		5 880			
	0.00	0.00	1.00		3,003			
	0.00	0.00	2.00		1 000			
1. ( U) POST DUCTORAL ASSOCIATES	0.00	0.00	2.00		1,000			
2. ( 0) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	0.00	0.00	0.00					
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5. ( U) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)					<u> </u>			
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					0,889			
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)					1,1/5			
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					8,064			
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDI	ING \$5,0	000.)						
Mark III ice coring system		\$	10,228					
TOTAL EQUIPMENT					10,228			
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSE	SSIONS	3)			1,800			
2. FOREIGN					4,500			
F. PARTICIPANT SUPPORT COSTS								
1. STIPENDS \$								
2. TRAVEL								
3. SUBSISTENCE								
4. OTHER0								
TOTAL NUMBER OF PARTICIPANTS ( <b>0</b> ) TOTAL PART	TICIPAN	IT COST	S		0			
G. OTHER DIRECT COSTS								
1. MATERIALS AND SUPPLIES					2.400			
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION					0			
3. CONSULTANT SERVICES					0			
4 COMPUTER SERVICES					0			
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6 OTHER					6/ /37			
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					101,000			
Direct Costs (rea)(SPECIFT RATE AND BASE)								
Direct costs (minus tunion, equipment) (Rate: 45.0000, Base: 74154)					22.260			
					33,309			
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)					135,175			
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS	SEE G	PG II.C.6	.j.)	+	<u> </u>			
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				\$	135,175	\$		
M. COST SHARING PROPOSED LEVEL \$ 0 AGREED LE		DIFFERE	NT \$					
PI/PD NAME			FOR	NSF US	E ONLY			
Bogdan P Onac		INDIR	ECT COS	ST RATE	E VERIFIC	CATION		
ORG. REP. NAME*	Da	ate Checked	Date	e Of Rate	Sheet	Initials - ORG		
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1 \*ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET

#### SUMMARY YEAR PROPOSAL BUDGET FOR NSF USE ONLY ORGANIZATION PROPOSAL NO. DURATION (months) University of South Florida Proposed Granted PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR AWARD NO. Bogdan P Onac Funds Requested By proposer Funds granted by NSF (if different) A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates NSF Funded Person-months (List each separately with title, A.7. show number in brackets) ACAD | SUMR CAL 1. Bogdan P Onac - Assistant Professor 0.00 0.00 1.00 \$ 5,889 \$ 2. З. 4. 5. **()** ) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE) 6. ( 0.00 0.00 0.00 0 7. ( 1) TOTAL SENIOR PERSONNEL (1 - 6) 5,889 0.00 0.00 1.00 B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS) 1,000 1. ( 0) POST DOCTORAL ASSOCIATES 0.00 0.00 2.00 **()** ) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.) 2. ( 0.00 0.00 0.00 0 **0**) GRADUATE STUDENTS 0 3. ( 4. ( 0) UNDERGRADUATE STUDENTS 0 5. ( 0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY) 0 6. ( **0**) OTHER 0 TOTAL SALARIES AND WAGES (A + B) 6,889 C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 1,175 TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C) 8,064 D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.) TOTAL EQUIPMENT 0 E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS) 1,800 2. FOREIGN 2.200 F. PARTICIPANT SUPPORT COSTS 0 1. STIPENDS \$ -0 2. TRAVEL 0 3 SUBSISTENCE 0 4 OTHER TOTAL NUMBER OF PARTICIPANTS **0**) TOTAL PARTICIPANT COSTS 0 G. OTHER DIRECT COSTS 1. MATERIALS AND SUPPLIES 500 2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION 0 3. CONSULTANT SERVICES 0 4. COMPUTER SERVICES 0 5. SUBAWARDS 5,228 6. OTHER 53,297 TOTAL OTHER DIRECT COSTS 59,025 H. TOTAL DIRECT COSTS (A THROUGH G) 71,089 I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) Direct Costs (excludes tuition) (Rate: 47.0000, Base: 58814) 27,643 TOTAL INDIRECT COSTS (F&A) J. TOTAL DIRECT AND INDIRECT COSTS (H + I) 98,732 K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.C.6.j.) 0 L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) \$ 98.732 \$ M. COST SHARING PROPOSED LEVEL \$ **AGREED LEVEL IF DIFFERENT \$** 0 PI/PD NAME FOR NSF USE ONLY INDIRECT COST RATE VERIFICATION Bogdan P Onac ORG. REP. NAME\* Date Checked Date Of Rate Sheet Initials - ORG

2 \*ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET

#### SUMMARY YEAR PROPOSAL BUDGET FOR NSF USE ONLY ORGANIZATION PROPOSAL NO. DURATION (months) University of South Florida Proposed Granted PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR AWARD NO. Bogdan P Onac Funds Requested By proposer Funds granted by NSF (if different) A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates NSF Funded Person-months (List each separately with title, A.7. show number in brackets) ACAD | SUMR CAL 1. Bogdan P Onac - Assistant Professor 0.00 0.00 1.00 \$ 5,889 \$ 2. З. 4. 5. **()** ) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE) 6. ( 0.00 0.00 0.00 0 7. ( 1) TOTAL SENIOR PERSONNEL (1 - 6) 5,889 0.00 0.00 1.00 B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS) 1,000 1. ( 0) POST DOCTORAL ASSOCIATES 0.00 0.00 2.00 **()** ) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.) 2. ( 0.00 0.00 0.00 0 **0**) GRADUATE STUDENTS 0 3. ( 4. ( 0) UNDERGRADUATE STUDENTS 0 5. ( 0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY) 0 6. ( **0**) OTHER 0 TOTAL SALARIES AND WAGES (A + B) 6,889 C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 1,175 TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C) 8,064 D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.) TOTAL EQUIPMENT 0 E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS) 2,700 2. FOREIGN 3.000 F. PARTICIPANT SUPPORT COSTS 0 1. STIPENDS \$ -0 2. TRAVEL 0 3 SUBSISTENCE 0 4 OTHER TOTAL NUMBER OF PARTICIPANTS **0**) TOTAL PARTICIPANT COSTS 0 G. OTHER DIRECT COSTS 1. MATERIALS AND SUPPLIES 0 2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION 300 3. CONSULTANT SERVICES 0 4. COMPUTER SERVICES 0 5. SUBAWARDS 5,241 6. OTHER <u>28,0</u>08 TOTAL OTHER DIRECT COSTS 33,549 H. TOTAL DIRECT COSTS (A THROUGH G) 47,313 I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) Direct Costs (excludes tuition) (Rate: 47.0000, Base: 36024) 16,931 TOTAL INDIRECT COSTS (F&A) J. TOTAL DIRECT AND INDIRECT COSTS (H + I) 64,244 K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.C.6.j.) 0 L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) \$ 64.244 \$ M. COST SHARING PROPOSED LEVEL \$ **AGREED LEVEL IF DIFFERENT \$** 0 PI/PD NAME FOR NSF USE ONLY INDIRECT COST RATE VERIFICATION Bogdan P Onac ORG. REP. NAME\* Date Checked Date Of Rate Sheet Initials - ORG

**3 \*ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET** 

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University of South Florida			FUSAL	NO. DO		Granted		
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Rondan P Onac		^		0.				
A SENIOR PERSONNEL: PI/PD Co-PI's Faculty and Other Senior Associates		NSF Fund	ed	Fund	s	Funds		
(List each separately with title, A.7. show number in brackets)	CAL	ACAD	SUMB	Requeste propos	ed By ser	granted by NSF (if different)		
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6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)	0.00	0.00	0.00		0			
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TOTAL SALARIES, WAGES AND FRINGE DENEFTTS (A + D + C)		20.)		2	4,192			
D. EQUIPMENT (LIST TEM AND DOLLAR AMOUNT FOR EACH TEM EXCEED)	ט,כב טאוו <b>מ</b>	.)	10.000					
	4	)	10,228					
TOTAL EQUIPMENT				1	0,228			
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSE	SSIONS				6,300			
2. FOREIGN					9,700			
				-				
F. PARTICIPANT SUPPORT COSTS								
1. STIPENDS \$								
2. TRAVEL 0								
3. SUBSISTENCE								
4. OTHER								
TOTAL NUMBER OF PARTICIPANTS ( <b>0</b> ) TOTAL PART	TICIPAN	T COSTS	3		0			
G. OTHER DIRECT COSTS								
1. MATERIALS AND SUPPLIES					2,900			
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION					300			
3. CONSULTANT SERVICES					0			
4. COMPUTER SERVICES					0			
5. SUBAWARDS				2	0,846			
6. OTHER				L 2				
				14	5.742			
				14 16	5,742 9.788			
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H. TOTAL DIRECT COSTS (A THROUGH G)				14 16 22	5,742 9,788 0,208			
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H. TOTAL DIRECT COSTS (A THROUGH G) I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TOTAL INDIRECT COSTS (F&A)				14 16 22	5,742 9,788 0,208 7 943			
H. TOTAL DIRECT COSTS (A THROUGH G) I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TOTAL INDIRECT COSTS (F&A) I. TOTAL DIRECT AND INDIRECT COSTS (H + 1)				14 16 22 7 20	5,742 9,788 0,208 7,943 8 151			
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H. TOTAL DIRECT COSTS (A THROUGH G) I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TOTAL INDIRECT COSTS (F&A) J. TOTAL DIRECT AND INDIRECT COSTS (H + I) K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) M. COST SHAPING REOPORCED LEVEL &	S SEE GF	PG II.C.6	j.)	14 16 22 7 29 \$ 29	5,742 9,788 0,208 7,943 8,151 0 8,151	\$		
H. TOTAL DIRECT COSTS (A THROUGH G) I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TOTAL INDIRECT COSTS (F&A) J. TOTAL DIRECT AND INDIRECT COSTS (H + I) K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) M. COST SHARING PROPOSED LEVEL \$ <b>0</b> AGREED LE	SEE GF	PG II.C.6	j.) NT \$	14 16 22 7 29 \$ 29	5,742 9,788 0,208 7,943 8,151 0 8,151	\$		
H. TOTAL DIRECT COSTS (A THROUGH G) I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TOTAL INDIRECT COSTS (F&A) J. TOTAL DIRECT AND INDIRECT COSTS (H + I) K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) M. COST SHARING PROPOSED LEVEL \$ <b>0</b> AGREED LE PI/PD NAME Paradag B Orage	SEE GF	2G II.C.6	j.) NT \$ FOR N	14 16 22 7 29 \$ 29	5,742 9,788 0,208 7,943 8,151 0 8,151 DNLY	\$		
H. TOTAL DIRECT COSTS (A THROUGH G) I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TOTAL INDIRECT COSTS (F&A) J. TOTAL DIRECT AND INDIRECT COSTS (H + I) K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) M. COST SHARING PROPOSED LEVEL \$ <b>0</b> AGREED LE PI/PD NAME Bogdan P Onac ORG REP. NAME*	S SEE GF	PG II.C.6 IFFEREI INDIRE	j.) NT \$ FOR N ECT CO9	14 16 22 7 29 \$ 29 \$ 29	5,742 9,788 0,208 7,943 8,151 0 8,151 0 8,151 0 NLY /ERIFIC	\$ CATION		

C \*ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET

## **Budget Justification**

### A. Senior Personnel

One month of summer salary is requested in years 1 through 3 for Dr. Onac to oversee the drilling of ice core and sampling of speleothems, stable isotope, and supervision of research activities of an undergraduate and one graduate student.

## **B.** Other Personnel

Funds are requested in years 1 to 3 for two post-doctoral associates (one summer month/year for each one).

## C. Fringe Benefits

Fringe benefits are calculated at 18.58% for Dr. Onac. Other Personnel (Post Doctoral Associates) fringe rate is 8.15%.

## **D.** Permanent Equipment

We request \$10,228 for the purchase of a 7.25-cm diameter Mark III ice coring system, which includes the engine drive, drill adapter, cutting bit, and 30 m of auger flights.

## E. Travel

International travel funds for the first year are requested for Dr. Onac, Dr. Dorale, and the graduate student to cover the flight costs to Romania. All travel and fieldwork within Romania will be covered from current grants to Dr Onac, Dr. Constantin and Persoiu (see Current and Pending Grants and also Supplementary Documentation). During years 2-3 we request international travel funds for Drs. Onac and Dorale, and graduate student to attend the European Geosciences Union meeting and the cost of travel to Tampa for Dr. Tamas (post doctoral associate) to work and prepare manuscripts fro publication. Roundtrip airfares from US to Europe are estimated at \$1,000 per person based upon average rates posted on www.orbitz.com.

We do request funds for domestic travel for 2 scientists and a graduate student per year to travel to national meetings (Fall AGU or GSA) to present research results. Registration, roundtrip airfare, and hotel are estimated at \$900 per person, per meeting.

## G. Other Direct Costs

## G. 1. Materials and supplies

The materials and supplies budget reflects funds necessary to purchase specific equipment (rope, crampons, ice screws) and sampling containers. The request for materials and supplies is lower in the second year and null in the third year when we spend less effort on laboratory work and more on scientific analysis and publication.

Funds are requested for year 1 to purchase 5,000 plastic containers (2 ml) @ \$ 360 for sampling the ice core for stable isotope analyses. Fifty-two plastic racks with lids @ \$770 are needed to safely transport and/or ship the samples. Zippit bags (pack of 500 @ \$205) are required for collecting various solid samples during fieldwork. A 60-m long rope ( $\emptyset$  10 mm) worth \$108, two pairs of crampons @ \$200 each, and six ice screws (\$80 each) are needed to access remote parts of the cave glacier.

The funds requested for the second year will cover the costs for 750 plastic containers (0.6 ml) @ \$124 to store calcite powder samples for stable isotope analyses, racks (with lids) @ \$257 and petrographic microscope slides and glass coverslips @ \$73 used to manufacture thin section for crystallographical studies of calcite fabric in speleothems.

#### **G. 2.** Publications costs

The amount requested for the third year represents costs of reprints and page charges.

G. 5. Subcontracts (see Budget Justification for Dr. Jeffrey A. Dorale)

#### G. 6. Other

## 6a. Tuition

Three years worth of graduate student in-state tuition is requested for a Ph.D. student (6048 = 252 per credit \* 24 credits/year) and two years undergraduate, in-state student tuition (9999 = 111 per credit \* 9 credits/year).

#### **6b.** Analytical Costs

This project requires large numbers of isotope measurements, which we have budgeted under the *Other* category.  $\delta^{18}$ O and  $\delta$ D are required for ice samples (~1,250) collected at 1 cm interval from the ~25 m long ice core. Here, we request funds to measure the upper part of the ice core in the first year (2,500 samples \* \$30/sample for both analyses = \$37,500) and the lower part in the second year (2,500 samples \* \$30/sample = \$37,500). The trace gases (CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) will be measured on the upper 10 m of the ice core (1,000 samples @ \$17.5/sample = \$17,500) and the plan is to analyze 5 m in the first years and the other 5 m in year 2. Because of the large number of samples needed, we established collaboration with two laboratories (University of Bern and University of Idaho) that can handle our required throughput.

Funds are requested to support the costs for 20 AMS <sup>14</sup>C datings (@ \$502/sample = \$10,040) on organic material extracted from the ice. The measurements will be done at the Gliwice Radiocarbon Laboratory in Poland.

We have access to oxygen and carbon stable isotope facilities with Thermo Finnigan-MAT Delta-Plus and Finnigan-MAT 251 mass spectrometers equipped with Kiel devices at three localities: at College of Marine Sciences at the University of South Florida (USF), University of Graz, and Czech Geological Survey. The cost at each facility is \$24/sample. Our project requires 1,500 oxygen and carbon measurements on two speleothems at 0.5-mm resolution. We request funds in the third year for 750 samples to be measured at USF (\$18,000). The remaining 750 analyses are covered from Dr. Onac's current Romanian grant and will be performed at the other two facilities (see letter of support).

To better understand the isotopic signal from ice and speleothems,  $\delta^{18}$ O and  $\delta$ D in precipitations and cave drip waters are required. For this purpose, monthly water samples will be collected outside the cave over 3 years time interval (36 samples \* \$30 for both

isotopes/sample = \$1,080). The same analyses are requested for cave drip waters collected monthly for two years period in two locations (in the warm and glacial zone) within the cave (96 samples \* \$30 for both analyses = \$2,880).

## I. Indirect Costs

Indirect costs are 45% in the first year and 47% in years 2-3 of all requested direct costs, except for equipment.

## 6b. Postage

Funds (\$1,100) are requested to mail part of the samples to different laboratories.

## **Budget Justification**

## A. Senior Personnel

One month of summer salary is requested in the first year and half of a summer month in years 2 and 3 for Dr. Dorale to oversee the drilling of ice core and sampling of speleothems, and for the U/Th work.

## C. Fringe Benefits

Fringe benefits for Dr. Dorale are calculated at 27% (year 1), 28% (year 2), and 28.3% (year 3).

## I. Indirect Costs

Indirect costs are calculated at 47.5% of all requested direct costs, except for equipment.

## **Current and Pending Support**

(See GPG Section II.C.2.h for guidance on information to include on this form.) The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal. Other agencies (including NSF) to which this proposal has been/will be submitted. Investigator: Bogdan Onac Support: Current □ Pending □ Submission Planned in Near Future □ \*Transfer of Support Project/Proposal Title: Paleoclimatic reconstructions based on interdisciplinary studies of ice deposits from caves in Romania Ministry of Education and Research, Romania Source of Support: 21,870 Total Award Period Covered: Total Award Amount: \$ 01/01/06 - 12/31/08 Romania Location of Project: Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 2.00 Sumr: 0.00 Current Pending Submission Planned in Near Future Transfer of Support Support: Project/Proposal Title: Rapid climate oscillations recorded in karst deposits from Romania as revealed by isotopic and palaeomagnetic proxies **Ministry of Education and Research, Romania** Source of Support: **183.000** Total Award Period Covered: Total Award Amount: \$ 10/12/05 - 06/30/08 Location of Project: Romania Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 1.00 Support: □ Current □ Pending □ Submission Planned in Near Future □ \*Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ Total Award Period Covered: Location of Project: Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: □ Pending □ Submission Planned in Near Future Support: □ Current □ \*Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ **Total Award Period Covered:** Location of Project: Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: Support: □ Current □ Pending □ Submission Planned in Near Future □\*Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ Total Award Period Covered: Location of Project: Person-Months Per Year Committed to the Project. Acad: Summ: Cal: \*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.

## **FACILITIES, EQUIPMENT & OTHER RESOURCES**

**FACILITIES:** Identify the facilities to be used at each performance site listed and, as appropriate, indicate their capacities, pertinent capabilities, relative proximity, and extent of availability to the project. Use "Other" to describe the facilities at any other performance sites listed and at sites for field studies. USE additional pages as necessary.

Laboratory:	Purposefully designed lab facilities for high-resolution stable isotope and trace elements analyses (listed below)
Clinical:	
Animal:	
Computer:	
Office:	
Other:	Clean room for chemical separation of U and Th. Clean room with appropriate exhaust capabilities, which house the alpha spectrometer listed below. This facility was designed for quick and basic uranium-series measurements. Stable isotope lab facilities at the University of Idaho, Czech Geological Survey and University of Graz
MAJOR EQUIPMENT capabilities of each.	: List the most important items available for this project and, as appropriate identifying the location and pertinent

University of South Florida: (1) Perkin Elmer Optima 2000 ICP-OES, (2) Two Finnigan MAT DeltaPlus XL mass spectrometers that have wide-ranging capabilities in terms of stable isotope ratio analysis (St. Petersburg campus of USF).

**OTHER RESOURCES:** Provide any information describing the other resources available for the project. Identify support services such as consultant, secretarial, machine shop, and electronics shop, and the extent to which they will be available for the project. Include an explanation of any consortium/contractual arrangements with other organizations.

Czech Geological Survey: Finnigan MAT 251 and Geo 20-20 mass spectrometers (20% available for the project - operated by Dr. Karel Zak). We also have agreements for measuring the oxygen, carbon, and hydrogen stable isotope ratios in ice or/and speleothems at University of Graz (Dr. Ana-Voica Bojar) using a Finnigan MAT Delta Plus and University of Idaho (Benjamin Miller) on two rationing mass spectrometers (Delta+XP and Delta+) if our in-house facilities become overloaded.

Continuation Page:

#### **OTHER FACILITIES (continued):**

(Austria).

#### **OTHER RESOURCES (continued):**

The mass spectrometric U-Th dating of speleothem sub-samples will be done at Taiwan National University in collaboration with Dr. Chaun-Chou Shen.

The bulk U/Th analyses will be performed at the Romanian Academy, Speleological Institute on an Octete Plus (Ortec) Alpha Spectroscopy Workstation (60% available for the project and will be operated by two of the post doctoral associates).