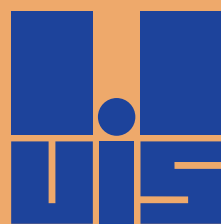




Proceedings of the
17th
International
Congress of
Speleology,
Sydney 2017

Volume One



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de Spéléologie



**17th INTERNATIONAL
CONGRESS OF SPELEOLOGY**

Sydney, NSW, Australia

July 22–28, 2017

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VOLUME 1

Edited by

Kevin Moore

Susan White

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Cover photo : Keir Vaughan-Taylor on Lake 2, Koonalda Cave, Nullarbor Plain. (Photo by Kevin Moore)

Back Cover : The Khan and Beagum in Kubla Khan Cave Tasmania (Photo by Garry K. Smith)

Contents

The contribution of cave sites to the understanding of Quaternary Australian megafauna records. Elizabeth Reed	1
Cave Diving in Australasia K. G. Smith and R. Harris	2
Australian Karst – Caves in an Ancient Land Rejuvenated John Webb	6
Archaeology and Palaeontology in Caves	
Timing Of Fossil Emplacement At Toca Da Boa Vista Cave System In Northeastern Brazil Augusto S Auler	13
Dating Paleolithic cave art in Shulgan-Tash cave, Ural, Russia Dublyansky Y., Moseley G.E., Spötl C., Liakhnitsky Y., Cheng H., Edwards R.L.	14
Copper Age ceramics from the Cerișor Cave (Southern Carpathians, Romania) Giurgiu, Alexandra; Ionescu, Corina; Tamas, Tudor; Hoeck, Volker; Roman, Cristian	18
Differential preservation of vertebrates in Southeast Asian caves Julien Louys, Shimona Kealy, Sue O'Connor, Gilbert James Price, Stuart Hawkins, Ken Aplin, Yan Rizal, Jahdi Zaim, Mahirta Mahirta, Daud Tanudirjo, Joseph Bevitt, Wahyu Dwijo Santoso, Ati Rati Hidayah, Agus Trihascaryo	18
Forensic Speleology – Exploration of caves containing WW2 human remains in Slovenia Andrej Mihevc	19
Bone-Hunters: exploration, analysis and interpretation of sub-fossil remains from Jenolan Caves, Australia ^{1,2} Anne M. Musser	23
Palaeontology Of Northeastern Australian Caves Gilbert J. Price, Jonathan Cramb, Julien Louys, Yue-Xing Feng	25
Nova spilja (New Cave) from 1882 - in Croatia Boris Watz	29
A Speleo-Archaeology Study Of Kali Banjar Underground River: Approach On The Research Of Site Formation Procces M. Wishnu Wibisono	30
Australian Caves and Karst	
“Fatuk-Kuak Hosi Timor Lorosaé”: Caves Of Timor-Leste Freire, M. ¹ , Pinto, P. ² , Soares, M. ³ , Medeiros, S. ⁴ , Reboleira, A.S.P.S. ^{1,5} , Reis, A. ² , Gomez, M. ⁶	34
Pocket valleys on the escarpments of the Nullarbor Plain, southern Australia, and their potential for palaeoenvironmental reconstruction Matej Lipar ¹ , Mateja Ferk ¹ , Susan White ²	39
Notes from the northern Nullarbor Ian Lutherborrow, Catherine Brown	42

Karst in Southern Bali and in Nusa Penida, Sunda Islands, Indonesia Claude Mouret	43
Flank Margin Cave Development and Tectonic Uplift, Cape Range, Australia John Mylroie, Joan Mylroie, William Humphreys, Darren Brooks and Greg Middleton	48
Eastern Australian Karsts and European Karsts: Some Comparisons Robert Armstrong Osborne	50
Caves of the Nullarbor – Their nature and setting. Henry Shannon	51
 Biospeleology, Evolution, Ecology and Problems	
Karstic Cave: Life and Soil Environment Angel A Acosta-Colón	56
Water Quality Evaluation of Chimachida Rimstone Pools in Akiyoshi Cave, Japan, Using Physicochemical and Biological Index Eri Ando	56
Disturbance caused to cave-roosting bats during ecological monitoring: implications for researchers and cavers Amanda Bush, Lindy Lumsden, Yvonne Ingeme, Christa Beckmann, Peter Biro	57
Faunal Diversity On Arid Lands Caves In The Sonoran Desert, Mexico M. C. Luis Omar Calva Pérez & Dra. Reyna A. Castillo-Gámez	58
Taxonomic review of the cave-dwelling springtail family Tomoceridae (Collembola) in Korea Gyu Dong Chang, Jae Won Kim, Young Gun Choi and Kyung Hwa Park	65
The Gcwihaba Caves Research Project: Past, present and future undertakings Gerhard du Preez, Hendrika Fourie, Roger Ellis and Gerhard Jacobs	68
Invertebrate and vertebrate cave fauna records for the Appalachian Valley and Ridge Annette Summers Engel, Matthew L. Niemiller, Kirk S. Zigler, Charles D.R. Stephen, Evin T. Carter, Audrey T. Paterson, Sarah W. Keenan, Steven J. Taylor	71
Starving In The Dark: The Impact Of Ultra-Small Cells On The Microbial Community Of The Wind Cave Lakes Olivia S. Hershey, Kayla A. Calapa, Hazel A. Barton	76
Tropical karst as an island of biodiversity: Melody Rocks, Cape York Peninsula, Australia Tim Hughes, Chris Clague, Roger B Coles, Bruce Thomson, Olivia Whybird	79
Observations of the first stygobiont snail (Hydrobiidae, <i>Fontigens</i> sp.) in Tennessee Sarah W. Keenan, Audrey T. Paterson, Matthew L. Niemiller, Michael E. Slay, Stephanie A. Clark, and Annette Summers Engel	80
Active Surveillance of Coronaviruses and Paramyxoviruses in Korean bats in 2016 Hye Kwon Kim, Yong Gun Choi, Sun-Woo Yoon, Ji Yeong Noh, Doo-Jin Kim, Moo-Seung Lee, Ji-Hyung Kim and Dae Gwin Jeong	84
First record of the Order Palpigradi Thorell, 1888 (Arachnida) from South Korea Jae-Won Kim, Gyu-Dong Chang, Young-Gun Choi	87
Microhabitat Distribution Of Invertebrates In White Cave, Mammoth Cave National Park, Usa Kathleen H. Lavoie, Ashley Huang, And Cassie Huang	88

Monitoring subterranean microbats in south-eastern mainland Australia Doug Mills	89
Seasonal Variations in Species Abundance and Impact of Large-Scale Visitation in Robber Baron Cave, Texas Evelynn J. Mitchell, Genne Liu, Melissa L. Karlin	90
Subterranean and surface cryptopid centipede diversity in Western Australia. Timothy A Moulds, Joel Huey, Mia Hillyer, Juliane Waldock, Mark S Harvey	95
Environmental metagenomics of the chemolitho-autotrophically based ecosystem of Ayalon Cave, Israel Audrey T. Paterson, Oren Kolodny, Israel Na'aman, Amos Frumkin, Annette Summers Engel	95
Iron-rich rocks: A little recognized habitat for troglifauna colonization Gustavo A Soares, Augusto S Auler	96
Life in Darkness – a Biospeleological Project in the Bavarian Alps Bärbel Vogel, Stefan Zaenker, Dr. Anne Ipsen, Andreas Wolf, Dr. Friedhart Knolle,	97
Cave Animal Of The Year – From National To International? Bärbel Vogel, Stefan Zaenker, Christian Zaenker, Dr. Anne Ipsen, Andreas Wolf, Dr. Friedhart Knolle	99
White-Nose Syndrome And Australian Bats – What Is The Risk And What Can We Do? Keren Cox-Witton, Rachel Iglesias, Peter Holz, Jasmin Hufschmid, Rupert Woods	102
Monitoring a Bat Maternity Cave in South-eastern Australia Using Remote Technology Yvonne Ingeme, Amanda Bush, Lindy Lumsden and Reto Zollinger	105
Cave and Karst Management and Education The Journey to Preserve Puerto Rico's Santa Rosa Cave System Miguel A Babilonia	107
Management of karst environments within NSW parks and reserves Andrew C. Baker	108
Conveying the importance of stromatolites to self-guided tourists in Nettle Cave, Jenolan, NSW. E. V. Barlow	110
New Materials, Techniques And Technologies For Best Practices In Show Caves Management Jean-Pierre Bartholeyns	115
Student and Public Engagement through Cave Microbiology Research at Thompson Rivers University, Canada Naowarat Cheeptham	119
One Of Earth's Special Places Deborah Craven-Carden, Chaka Chirozva.	124
The denunciation as a tool to protect the speleological heritage in Brazil Leda de Almeida Zogbi, Gustavo Feitosa Vieira Monteiro	130
Stalagmite isotopic record from Mallorca (Western Mediterranean) over the last 120 ka: paleoclimatic implications Dumitru Oana-Alexandra, Onac Bogdan P., Polyak Victor J. , Wynn Jonathan G., Asmerom Yemane, Fornós Joan J.	131

Proposal For Valuing Geosites From João Guimarães Rosa's Books: Creating The "Sertões De Minas Gerais" Geopark In Brazil Vânia Kele Evangelista, Luiz Eduardo Panisset Travassos	132
Evaporite karst of the Emilia-Romagna Region (Italy): why should they become a UNESCO World Heritage? Paolo Forti	133
Speleo Education In Hungary Hegedűs, Gyula	138
International Cave Conservation and Restoration Course in Brazil Val Hildreth-Werker, Jim C. Werker, Luciana Alt, Vitor Moura	143
Caves And Ancient Human Life Irawati Yuniat	148
World-Wide Largest Biosphere Reserve On Sulphate Karst And The Schlotten Caves – Endangered Geo- And Biodiversity Hotspots In The South Harz, Germany Friedhart Knolle, Stephan Kempe, Bärbel Vogel, Hildegard Rupp	149
The Detection of Human Activities' Impact on Show Caves Environment in Pacitan, Indonesia Isma Dwi Kurniawan, Cahyo Rahmadi, Tiara E. Ardi, Ridwan Nasrullah, Muhammad Iqbal Willyanto, Suhandi Rahayu	153
Preliminary Observations on Tropical Bat Caves as Biogeochemical Nitrogen Sinks Donald McFarlane, Joyce Lundberg, Guy van Rentergem	157
2013 to 2016 speleological explorations in Khammouane, Laos Claude Mouret and Jean-François Vacquié	161
Contribution to cave tourism promotion in Laos Claude Mouret	165
Use of cave environments by vertebrate animals: examples from Jenolan Caves, Australia Anne M. Musser	170
<i>Caver Quest</i> – A New Paradigm in Cave Interpretation Steve Peerman, Dr. Ron Lipinski	174
The Application of a Cave Ecosystem Profile to Anjani Cave in Karst Jonggrangan, Central Java, Indonesia Hilary Reinhart, Fajar Fathur, Agustin Erviana, Yoyon Arifta Yudha Trias, Rifqi Harahap, Shabrina Tamimi, Erlyn Mattoreang, Rezky Rahmawan, Nurul Hakiki, Yanik Eri Mashlikhah, Wahyu Kuncoro, Rizky Fauzan	179
Evaluating the Status of Cave and Karst Protection in the United States of America Seiser, Patricia E.	183
Methodological Planning For The Public Use Of Caves And Karst Based On Spatial Analysis Maps Marcos Otavio Silverio	184
It Was A Dark And Stormy Night When The Crickets Returned: Recovery Of Biota After Cleaning A Heavily Impacted Commercial Cave (Crystal Cave, Kutztown, Pa, Usa) Soroka, Douglas, Lavoie, Kathleen	187
Missouri Cave Database – a comprehensive tool for cave management. Michael Sutton and Scott House	189
Cave access challenges at Sistema Huautla, Mexico Charles William Steele	192

Geopark Proposal At The Arcos-Pains Speleological Unit, Minas Gerais, Brazil Mariana Barbosa Timo, Luiz Eduardo Panisset Travassos	193
White-nose Syndrome Response at Mammoth Cave National Park (USA) Rickard S. Toomey, III	194
Nakanai Cave/Karst Country, New Britain, Papua New Guinea: An Anthropological Perspective Roxanne Tsang, Matthew Leavesley, Jason Kariwiga, Patrick Kontorea, Iggie Matapia, Matthew Kelly, Jim Specht, Michael Wood, Colin Filer, Jennifer Gabriel, Simon Foale, and Susan McIntyre-Tamwoy	198
Smart Monitoring of Cave Habitats - the VdHK Smartphone App Bärbel Vogel, Stefan Zaenker, Christian Zaenker, Dr. Anne Ipsen, Andreas Wolf, Dr. Friedhart Knolle	202
Karstcare - Cavers Looking After Caves And Karst David Wools-Cobb	204
Cave Climate and Palaeoclimate Records	
Heat Waves In Caves: A Useful Tool Arrigo A. Cigna	209
A $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ guano-derived 1200 year record of hydroclimatic change influenced by the North Atlantic Oscillation: NW Romania Daniel Martin Cleary, Bogdan Onac, Jonathan Wynn, Ferenc Forray, Ioan Tantau	213
Sourcing Carbon Dioxide Gas In Karst Systems Fernandez-Cortes, A, Cuezva, S, Pérez-López, R, Matthey, D P, Hernández-Vicente, I, Bourges, F, Fisher, R, Cañaveras, J C, Calaforra, J M, Sanchez-Moral, S	214
Reconstruction of lapse rates during the Pleistocene-Holocene transition from Swiss stalagmites by noble gases analysis Elaheh Ghadiri, Matthias S. Brennwald, Dominik Fleitmann and Rolf Kipfer	219
Extreme Seasonal Fluctuations Of Carbon Dioxide In The Cave Atmosphere Of Cova De Sa Font (Sa Dragonera Islet, Balearic Islands, Spain) Angel Ginés, Antoni Mulet, Marta Rodríguez-Homar, Mateo Vadell, Enrique P. Sánchez-Cañete and Joaquín Ginés	220
Experiments on short-time human impact on the cave environment: Monitoring Grønligrotta Show Cave, Rana, North Norway Hildegunn Grindheim, Rannveig Øvrevik Skoglund, Sverre Aksnes, Stein-Erik Lauritzen	224
Microclimate Monitoring At Rei Do Mato Cave, Sete Lagoas, Minas Gerais, Brazil: Preliminary Results Márcia Silva Leão, Luiz Eduardo Panisset Travassos	224
Peculiar CO ₂ values in a Hungarian cave with lower and upper entrances Szabolcs Dr. Leél-Őssy, József Stieber	225
Speleogenesis in Stockyard Gully National Park and Beekeepers Nature Reserve, Western Australia Matej Lipar, John A. Webb,	226
Timing of Pliocene sea-level high-stands in western Mediterranean using U-Pb ages of cave deposits from Mallorca Island Bogdan P. Onac, Victor J. Polyak, Joan J. Fornós, Oana-Alexandra Dumitru, Yemane Asmerom, Joaquín Ginés, Angel Ginés	230
High-resolution examination of drought and pluvial events in southwestern USA stalagmites V. J. Polyak, Y. Asmerom, M.S. Lachniet, P.P. Provencio	231

Microclimate Monitoring At Gruta Da Lapinha (Lapinha Cave), Sumidouro State Park, Minas Gerais, Brazil: Preliminary Results Luiz Eduardo Panisset Travassos, Márcia Silva Leão, Heros Augusto Santos Lobo	234
How convective cave ventilation affects speleothem growth Chris Waring	235
 Cave Mineralogy	
Secondary Minerals From Italian Sulfuric Acid Caves Ilenia Maria D'Angeli, Jo De Waele, Cristina Carbone, Mario Parise, Giuliana Madonia, Marco Vattano	237
Secondary minerals from halite caves in the Atacama Desert (Chile) De Waele Jo, Carbone Cristina, Sanna Laura, Vattano Marco, Galli Ermanno, Forti Paolo	242
Mineral- and fine-grain sedimentology of the Reingardslia karst, Rana, North Norway. Hege Kilhavn, Ida Marie Gabrielsen, Rannveig Øvrevik Skoglund & Stein-Erik Lauritzen	247
Adipocere as a Group IX cave mineral and precursor for calcification on bone Stein-Erik Lauritzen,	251
Ikaite in old and newly formed ice deposit of Scărișoara Ice Cave, Romania Bogdan P. Onac, Jonathan G. Wynn	252
Fe-oxide filaments interpreted as fossil bacteria in byproducts of hypogene speleogenesis V. J. Polyak, P.P. Provencio	253
Water travelling on the edge of Fringed Cave Shaws Jill Rowling	257
Mineralogy and origin of the 18 km-long Snowy River formation, Ft. Stanton Cave, New Mexico (USA) Michael Norman Spilde	261
Uricite From Gaura Țuranului, NW Romania Tudor Tamas, Alexandra Mihaela Giurgiu, Lucian Barbu-Tudoran, Bogdan Mureșan	262
The Microbiome Of Manganese Speleothems From Baia Lui Schneider Cave, Romania Tudor Tamas, Adrian-Stefan Andrei, Manuela Păușan, Horia Banciu	263
A Native Aluminum Occurrence In Roraima South Cave, Venezuela Franco Urbani, Bogdan P. Onac	264
Effects of photosynthesis and groundwater input on diel variations of electrical conductivity and calcite precipitation in Chaotian River, Guilin, China Cheng Zhang, Jinliang Wang, Qiong Xiao	265
 Exploration and Cave Techniques	
New Discoveries In The Splinter Section, Jewel Cave, South Dakota Dan Austin and Michael E. Wiles	267
Humba Cave Project—Cave expedition in Sumba Island, Indonesia Nodoka Baba, Yushiro Kuroki	270
Recent Explorations In The Xe Bang Fai Cave System, Laos Terry Bolger	275

Multi-faceted training of caver-explorer Anatoliy Bulychov, Tatyana Sorokina	278
Cave exploration in the Amari region of central Crete and its connection with Australian soldiers in the aftermath of the Battle of Crete. Paul Cadas	285
The Caves Of Armenia Charles G. Chavdarian	289
Caves in Bolikhamsai Province, Laos Yuriko Chikano	294
Paraíso Cave: a remarkable limestone cave system in the Brazilian Amazon Leda de Almeida Zogbi, Janice Muriel-Cunha, Augusto Sarreiro Auler, Francisco William da Cruz, Aécio Rodrigo Motta	297
“Lights in the Darkness” Project captures images of the most beautiful caves in Brazil. Leda de Almeida Zogbi, Allan Silas Calux, Annie Guiraud, Philippe Crochet, Mirjam Widmer, Kevin Downey	298
Caving and Cave Exploration in Pakistan Durrani, Hayatullah Khan, Brooks, Simon James	299
Recent progress in Polish cave exploration projects in Northern Limestone Alps Mateusz Golicz	303
New Findings In Underwater Exploration Of The Bjurälven Valley Caves Dmitri Gorski, Bo Lenander, Mats Fröjdenlund, Stina Gabrielsson, David Thor, Sami Paakkarinen	307
Sump Diving Exploration In Mammoth Cave, Jenolan Caves, Nsw Blue Mountains Ms Deborah A Johnston MBMSc (CogSc) BSc (Psych) BA (CogSc, Soc)	311
Common characteristics of successful sump diving projects, a story of Main Drain Cave, Utah, U.S.A. Jean Krejca	315
Cave Radio For Direction Finding And Communication Bo Lenander - SM5CJW	316
International Cave Search and Rescue Team Slovenia Maks Merela Marko Zakrajsek	320
Exploration of the Cliff Caves of the Nullarbor Milner SJ, Short RD, and Campbell AW.	321
Cave Exploration In Xiaonanhai Karst Area, Shaanxi Province, China Zdenek Motycka, Michal Filippi, Zhang Yuan Hai	325
New Exploration In Underwater Cave Systems In Riviera Maya, Mexico Zdenek Motycka	329
Characteristics Of Limestone Caves In The West Of Khuvsgul Lake, Northwestern Mongolia Kohei Noike, Koichi Morizumi, Avirmed Erdenedalai	331
Fort Stanton Cave: World-Class Steve Peerman	335
Caving Expedition To The Humpata Plateau, Angola Pinto, P., Freire, M., Andrade, R., Francisco, R., Serôdio, R.	340

Cave Exploration in Sangkulirang-Mangkalihat Peninsula, East Kalimantan-Indonesia Eko Haryono, Hilary Reinhart, Syaiful Effendi, Prastyo Adi Irianto, Wilda A. Fathoni, Tiara Esti Ardi, Achdiat Putera, Tri Setiawan, Muhammad Dayatullah, Yanti Sanda Rinding, Abraham Sulistiono	344
La Venta Association, 25 years of exploration projects and discoveries Francesco Sauro, Antonio De Vivo, Tullio Bernabei, Paolo Forti, Francesco Lo Mastro, Leonardo Piccini, Jo De Waele	350
Ten Years Of Prospecting, Exploration And Documentation Of Caves At Bulha D'água Region And Surroundings, Brazil Marcos Otavio Silverio, Alexandre Iscoti Camargo, Roberto Brandi	355
Cavity searching and 3D density mapping via muon tomography Gergely Surányi, Gábor Molnár, Gergely Gábor Barnaföldi, Gergő Hamar, László Oláh, Dezső Varga	358
Photographing New Zealand's subterranean wilderness Marcus Paul Thomas	359
Exploring for New Caves on the Nullarbor Plain, Australia Nicholas White, Ken Boland, Daryl Carr, Greg Leeder	360
 Extraterrestrial Caves	
Speleology As An Analogue To Space Exploration: Five Years Of Astronaut Training, Testing And Operations In The ESA CAVES Program Loredana Bessone, Jo De Waele, Francesco Sauro	364
A Theoretical Approach to Energy and Materials Flow and Consequent Biodiversity: Predictions for Caves on Earth and Other Planetary Bodies Penelope Jane Boston and Diana Northup	370
What if the "Seven Sisters" are not volcanic? A look at deep hypogene sinkholes in Arabia STEPHAN KEMPE	371
Digital Terrain Model (DTM) morphometry of sinuous pit chains and atypical pit craters related to colossal inflated lava tubes on Mars Francesco Sauro, Riccardo Pozzobon, Pierluigi De Berardinis, Matteo Massironi, Jo De Waele	375
 Geomicrobiology of Cave and Karst Environments	
Next-Generation Sequencing For Microbial Characterization Of Biovermiculations From A Sulfuric Acid Cave In Apulia (Italy) Ilenia M.D'Angeli, Jo De Waele, Maria Grazia Ieva, Stefan Leuko, Martina Cappelletti, Mario Parise, Valme Jurado, Ana Z. Miller, Cesareo Saiz-Jimenez	377
What's Up With Antibiotics In Caves? Barton, Hazel A, and Lowry, David S.	381
Microbial role in speleogenesis in a sulfidic aquifer Christian Clark, Jennifer Macalady	384
Exploring the microbial diversity featuring the geochemical complexity of the quartz-sandstone cave Imawari Yeuta, Auyan Tepui, Venezuela Daniele Ghezzi, Francesco Sauro, Hosam Mamoon Zowawi, Pei-Ying Hong, Martina Cappelletti, Leonardo Piccini, Davide Zannoni, Freddy Vergara, Jo De Waele	385
Biosignature potential in sulfur isotopes of cave gypsum Jennifer Macalady, Muammar Mansor, Matthew Fantle	392

Rock-powered life in the vadose zone at Wishing Well Cave, VA (USA) Jennifer Macalady, Lexi Golestani, Paul Winter, Zena Cardman, Uyen Nguyen	393
Preliminary Observations on Tropical Bat Caves as Biogeochemical Nitrogen Sinks Donald McFarlane, Joyce Lundberg, Guy van Rentergem	394
Cryptic Microbes In Cave Minerals Diana E. Northup	398
Can Fermenting Bacteria Drive Speleogenesis in Fe(III)-rich Rocks? Ceth W. Parker, John Senko, Ira D. Sasowsky, Augusto Auler, Hazel A. Barton	399
Chemoautotrophic microbial mats rich in nanowires at a gas-gas redox interface in Smelly Cave (Romania) Serban M Sarbu, Joost W. Aerts, Jean-François Flot, Kenneth H. Neelson, Casey Barr, Viorel Atudorei, Artur Ionescu, Bogdan P. Onac, Calin Baci, Rob van Spanning, Ferenc L. Forray, Radu Popa	401
Biogeography of microbes from caves in the Interior Low Plateau and Appalachians karst regions Annette Summers Engel, Audrey T. Paterson, Matthew L. Niemiller	402
Fungal diversity in caves and on hibernating bats in North America Vanderwolf KJ, DF McAlpine, and D Malloch	403
Cultivable Bacterial Diversity from Iron Curtain Cave in Canada Soumya Ghosh, Elise Paine, Rob Wall, Gabrielle Kam, Tanna Lauriente, Pet-Chompoo Sangarmangkang, Derrick Horne, Naowarat Cheeptham	405
Bacteria isolated from Bush Lake and Timber Lake, British Columbia, Canada exhibit antagonistic activities against <i>Pseudogymnoascus destructans</i> the causative agent of white-nose syndrome Soumya Ghosh, Robyn McArthur and Naowarat Cheeptham	406
 History of Speleology and Karst Research	
Honouring Personages: named caverns in Jubilee right-hand branch Kathleen Bellamy, Jimmy Y.M.Lim, Jenny Whitby	408
Cave Exploration During The Little Ice Age Greg Brick, Ph.D.	411
The Prehistory Of Cave Fauna Paradigms Greg Brick, Ph.D.	414
Cyprus caving history Bernard Chirol	415
The oldest cave maps in the world Bernard Chirol	417
Women Underground — A world history of female contribution in speleology Bernard Chirol	419
The Lost Pot of the Sinkhole of the River Rhône Bernard Chirol	420
Hermann Bock, A Forgotten Precursor Of Cave Meteorology Arrigo A. Cigna	423
Investigating Mammoth Cave during the American Civil War Joseph C. Douglas	426

Karst Studies in Australia – Jiří V. Daneš and his Australian travels John Dunkley, Bruce Welch & John Pickett	429
The Publications Exchange Working Group Trevor Faulkner ^{1,2}	430
Cavers For Cavers – 50 Years Of Uis Cave Rescue Commission Hegedus, Gyula	432
Is The Inscription Dated 1213 In Postojnska Jama Really The Oldest Known? Stephan Kempe	437
OPERATION “CAVE” – The East German Secret Service ‘Stasi’ and its focus on cavers and SPELEOLOGY	442 442
Friedhart Knolle, Bärbel Vogel, Andreas Wolf	
Karst And Caves Throught The Eyes Of The Brazilian Emperor, Dom Pedro II (1831-1889)	446
Luiz Eduardo Panisset Travassos, Sebastião Ricardo Machado Meireles	
Karst, Caves And Geodiversity In The “Travels In Brazil (1817-1820)” By Johann Baptist Von Spix And Carl Friedrich Philipp Von Martius	446
Luiz Eduardo Panisset Travassos, Marcella Cristiane Amaral Scotti	
The Karstological Subterranean Laboratory Of Bossea Cave (N Italy)	447
Vigna B., Peano G., Villavecchia E., De Waele J.	
50th Anniversary of the UIS	452
Boris Watz	
16th ICS Brno	452
Boris Watz	
Procedure And Organisational Structures Of The Rescue In The Riesending Cave	453
Andreas Wolf, Bärbel Vogel, Friedhart Knolle	
Perceptions And Recommendations After The Cave Rescue In Riesending Cave	456
Andreas Wolf, Bärbel Vogel, Friedhart Knolle	
Author Index	460

Preface

Welcome to the 17th International Congress of Speleology and we hope you enjoy the Congress and appreciate the papers presented here in the Proceedings. These Proceedings are issued by the 17th International Congress of Speleology (Speleo2107) on July 22-28, 2017 in Sydney, NSW, Australia.

The large number of papers and posters presented here represents a huge amount of work by the authors, the reviewers and the editorial team. There are about 250 oral paper presentations and 61 posters. This represents a huge number of received e-mails and a similar number of responses during the last 6 months, with a similar load of electronic files and over 800 printed pages of text. This is a large amount of interesting material concentrating on Cave and Karst matters.

The author's guidelines stipulated that the particular contributions should not exceed 6 pages of text and we were delighted to find that most authors prepared contributions close to this upper limit. This illustrates a clear willingness of the cavers and karst scientists to share their discoveries and research conclusions.

The presented contributions (abstracts/papers) stand for both oral and poster presentations as indicated in the headings. Contributions in each session are arranged alphabetically by the last name of the first author. All contributions were reviewed by invited reviewers. Assistance was given to improve the English expression for those whom English is not their primary language. This has improved the clarity and readability of the contributions. Unfortunately due matters out of our control this reviewing process took much longer than expected and the problems of lost emails and the vagaries of the internet added to the unfortunate delays.

Twenty two thematically different sessions three plenary lectures were scheduled to cover the whole range of subjects to be discussed within the wide scope of the 17th ICS. Low numbers of contributions for some sessions necessitated their grouping with others in the program but we have attempted to keep them separate here. The contributions are grouped into two separate volumes.

The volumes are published digitally and will be available on the Karst Information Portal. <http://digital.lib.usf.edu/karst>. There are very few copies printed in hard copy. This is partly due to issues of people travelling to Australia and needing to either carry bulky books or expensively post home. The printed copies are only in black and white whereas the digital are print quality full colour. In many cases it will be more cost effective for people to print from the data stick at home, and certainly much easier to transport.

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We apologize for the all mistakes that might have crept into various submissions, from various versions of the manuscripts and other related files and emails which passed through our computers. We hope that everybody finds interesting reading here and we wish that the whole publication (Volumes 1 & 2) is a valuable record of the 17th meeting of enthusiasts addicted to the fascination of the underground world.

Finally we thank all the authors for their contributions and the reviewers for their work in improving the text. Thank you everyone for their patience.

Enjoy!

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Sourcing Carbon Dioxide Gas In Karst Systems

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Abstract

Recent studies have demonstrated that caves may act as significant reservoir of CO₂ gas on an annual scale and may be acting as sinks for atmospheric CH₄ on a daily scale, which provides evidence that the subterranean atmosphere of karst systems may play a key role in regulating greenhouse gases in the atmosphere. In this study, we have measured CO₂ variability and carbon isotope composition of subterranean air in karst environments. The cave sites cover a spectrum of local climates (oceanic and continental), bedrock lithology, cave microclimatic conditions, ventilation pattern, geomorphological and speleogenesis types (epigenic and hypogenic caves). The potential mechanisms involved on the CO₂ dynamic of either soil or geogenic-derived CO₂ in subterranean atmospheres are discussed. The atmospheric air that is inhaled into dynamically ventilated epigenic caves then return to the lower troposphere as CO₂-enriched air, during periods with higher ventilation. The first samples obtained in an active hypogenic cave (Vapor cave) exemplify the potential releasing of CO₂ along the faults and in the fractures occurring in the carbonate rocks and its significant influence on the conditions of the adjacent soil and local atmosphere at exterior.

Keywords: carbon dioxide, methane, caves, carbon isotopes, karst, subsoil.

1. Introduction

The increasing concentration of greenhouse gases (GHGs) in the atmosphere and its relationship to the Earth's climate are deserving a special scientific attention focused on the identification and characterization of all possible sources, reservoirs and sinks of GHGs, in order to calculate more accurately the carbon greenhouse gases budget, mainly CO₂ and CH₄ (Ciais *et al.* 2013 and references therein). The subterranean atmospheres are key locations to be considered regarding the balance of atmospheric carbon. Karst settings are reported to cover between 12 and 25% of the land surface of the Earth mainly linked to outcrops of carbonates (Ford and Williams 2007). These areas are potentially capable of harboring underground air masses (e.g. caves) that are periodically renewed by interaction with the atmospheric boundary layer and directly influence their physicochemical properties.

Some previous tracing studies employing carbon isotopes (Frisia *et al.*, 2011; Garcia-Anton *et al.*, 2014 and 2017; among others) or an analytical approach addressing CO₂ fluxes (Cuezva *et al.*, 2011; Corinne *et al.*, 2013), have demonstrated that the deep soil air CO₂ is the main source of this gas in cave air in near-surface cavities (generally formed under an epigenic context). CO₂ air in some deeper caves results from the interaction of cave ventilation with a reservoir of CO₂-enriched ground air formed by the decay of organic matter washed down into the deeper unsaturated zone (Matthey *et al.* 2016) and held within the smaller voids and fissures of the bedrock-surrounding cave.

Caves formed by specific hydrogeochemical mechanisms of hypogene speleogenesis and their interaction, e.g. hydrothermal, sulfuric acid, mixing corrosion, dissolution of evaporites, dissolution in mixed sulfate-carbonate sequences (Klim-

chouck *et al.*, 2014; Chavez and Reehling, 2016) can harbour subterranean atmospheres with a distinctive gas composition with presence of abiotic CO₂ gas (formed by chemical reactions which do not directly involve organic matter), which are frequently mixtures of multiple sources. This composition results from the current activity or residual signs of some processes as degassing from CO₂-rich groundwater or deep-sourced (geothermal) CO₂.

The pathways and mechanisms that control the fluxes of CO₂ among atmosphere, soil and subsurface reservoirs in karst terrains have not been characterised to date from an overall view, i.e. including at the same time diverse geological, tectonic and hydrogeological environments in the data analysis process. Here, we put forward some general insights concerning the GHGs behaviour in the upper vadose zone of karst terrains, based on climatic and gas composition monitoring combined with geochemical tracing using the stable carbon isotopic signature ($\delta^{13}\text{C}$) of CO₂. This study contributes with new data and findings to define and characterize the biotic and abiotic processes that regulate the CO₂ dynamic in near-surface epigenetic and hypogenic caves and assess their interaction with the external atmosphere.

2. Sites, materials and methodology

Fieldwork based on tracking gases has been deployed in sites where authors maintain a comprehensive cave monitoring and sampling networks in place for air analysis of soil and subsurface. Here it is only presented four of the most outstanding cave sites that summarize a wide range of processes that regulate the consumption and storage of CO₂ and CH₄. Ojo Guareña cave (northern Spain) is a highly ventilated cave with large daily and climate-driven oscillations of CO₂ levels (680–1900 ppm/day) (Fernandez-Cortes *et al.*, 2015). Castañar cave

(central Spain) is a low-energy and quite isolated cave with very high thermal stability and poorly ventilated at daily scale (Fernandez-Cortes *et al.*, 2011). Pech Merle cave (southern France) is an example of cave atmosphere enriched in soil-derived CO₂ (1.4–2.8%) and depleted in O₂ (<19.5%), with clear evidences of stability of its underground microclimate since last two decades (Bourges *et al.*, 2014). Vapor cave (southeastern Spain) represents a particular case of chasm developed in a karstic area of active faulting with evidence of geogenic sources for CO₂ and CH₄, hydro-thermalism (38–43 °C), hypoxic conditions (O₂ ranging 17–18%), related to upwelling flow in or from the zone of fluid-geodynamic influence (Perez-Lopez *et al.*, 2016).

Spot air sampling was conducted in a predefined network of points spatially distributed inside each cave and exterior atmosphere. Soil air collection was also conducted at sites located vertically above each cave at a depth of 50 cm, near the bedrock–soil interface. Air samples were collected into 1 L Tedlar bags with lock valves and using a micro-diaphragm gas pump. Samples were obtained on a bi-monthly basis in Ojo Guareña and Castañar cave during more than annual cycle. Pech Merle and Vapor cave were sampled under, at least, two different meteorological seasons.

Bag samples were analyzed using a CRDS analyzer model G2201-i (Picarro Inc., Santa Clara, CA, USA) belonging to the National Museum of Natural Sciences (Spanish Research Council). The device was calibrated before each analysis session using synthetic gases with known concentrations. Further details about the methodological procedures can be found in Fernandez-Cortes *et al.* (2015). CO₂ mole fractions of samples were also measured independently in the greenhouse gas laboratory at Royal Holloway University of London with a Picarro G1301 CRDS analyzer, calibrated against the NOAA reference gases. The carbon isotopic ratio ($\delta^{13}\text{C-CO}_2$) of bag samples was measured in the RHUL lab in triplicate to high precision ($\pm 0.05\text{‰}$) by continuous flow gas chromatography isotope ratio mass spectrometry (CF GC-IRMS) (Fisher *et al.* 2006).

3. Results and Discussion

Figure 1 summarizes some prevailing processes once the dataset of gas concentrations (CO₂) and its carbon isotopic ratio were analyzed for the studied caves. The extrapolation down to the X-axis of the keeling functions (colored lines of Figure 1) gives the $\delta^{13}\text{C}$ for the CO₂ sources at each cave site (-26.16‰ at Ojo Guareña, -26.19‰ at Castañar, -23.08‰ at Pech Merle). These $\delta^{13}\text{C-CO}_2$ data confirm that CO₂ in shallow caves (Castañar and Ojo Guareña) results from mixing atmospheric air and CO₂ produced by microbial respiration in soils containing organic material from C3 vegetation (around -27‰ according to Amundson *et al.*, 1998, in contrast to the observed $\delta^{13}\text{C}$ values for C4 vegetation; approximately -14‰, O’Leary, 1988).

The $\delta^{13}\text{C}$ of the CO₂ source in Pech Merle is heavier than other caves despite of the woodland vegetation with a C3 pathway is predominant on the surface. This suggests that ground air is influenced by the decay of organic material washed down into the deep soil and unsaturated zone and it could be another important CO₂ source of this cave. The organic matter from soil can be transported by infiltration of water through fractures

and voids in the vadose zone immediate below the deepest layers of soil. The microbial decomposition of this organic matter leached from the soil produces air enriched in CO₂ and, undoubtedly, with a different isotopic composition from the CO₂ generated directly by modern-day soil. This CO₂ with a heavier $\delta^{13}\text{C}$ can then enter the cave through diffusion via cracks and fissures in the bedrock. Matthey *et al.* (2016) have also described this additional CO₂ source in Gibraltar caves and it seems to be also responsible for the high accumulation of this gas in Pech Merle, which is favoured by the prevailing low air renewal of this cave site. The high CO₂ concentration in Pech Merle (ranging 1.5–2.7%) determines the tendency to hypoxic conditions of the cave atmosphere due to a mole-to-mole replacement of O₂ by CO₂ in air (O₂ levels ranging 17.9–19.5%)”.

The grey-shaded area in Figure 1 shows the air-mixing model in shallow epigenic caves (e.g. Ojo Guareña and Castañar) between background atmosphere and a theoretical composition of pure CO₂ produced by microbial respiration in soil. The black-solid straight lines of the mixing area are labeled as % of pure additional CO₂ from soil remaining in the cave air and soil air. As the distance of the cave air samples from the y-intercept of the Keeling models increases, there is greater ventilation and greater influence of the external atmosphere. Conversely, when CO₂ concentration is high and $\delta^{13}\text{C}[\text{CO}_2]$ tends toward the y-intercept, the gas enters by diffusion and has a mainly edaphic origin. Cave air in highly ventilated sites as Ojo Guareña is well mixed with background atmosphere and the remaining soil-derived CO₂ is usually below 5% with a marked seasonal variation, except for air samples collected during summer months (from July to early September) when this percentage is above 10%. By contrast, air of poorly ventilated cave as Castañar the remaining soil-derived CO₂ is usually above 10%.

The black-solid curved arrows in Figure 1 show the kinetic fractionation trajectory of soil CO₂ due to its upwards diffusion to open atmosphere, modelled by a Rayleigh-type distillation process with a fractionation coefficient of 4.4‰ (based on the theoretical mass-dependent fractionation between ¹²CO₂ and ¹³CO₂ during diffusion, according to Camarda *et al.*, 2007). The Rayleigh equation is an exponential relation that describes the partitioning of isotopes between two reservoirs as one-reservoir decreases in size, in this case the CO₂ content in soil air. Each curve arrow starts from a soil air with a different percentage of remaining pure CO₂ produced by respiration in soil, i.e.; theoretical source of CO₂ (2% CO₂ and -27‰ $\delta^{13}\text{C}$), 20% remaining and 50% remaining, from the lower to upper arrow respectively. As an example, the upper curve arrow is labelled with the fraction of CO₂ remaining after Rayleigh fractionation associated to the diffusion process. Some cave air samples from Ojo Guareña and Castañar fit well to these diffusion curves, i.e. CO₂ of cave air tends to be heavier while its concentration almost no change, which could indicate a slight diffusion of this gas from the monitored areas of this cave to deepest or nearby locations of the vadose zone.

A distinctive case is represented by the air samples from Vapor cave, where the high concentration of CO₂ and its heavier $\delta^{13}\text{C-CO}_2$ (5.97‰ on average) result from a deep source of CO₂ in cave-air. The hypogene speleogenesis and the current

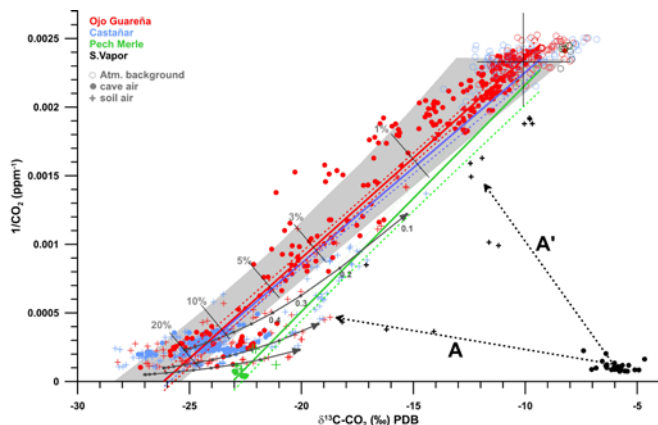


Figure 1. Keeling plot of $1/\text{CO}_2$ versus $\delta^{13}\text{C}-\text{CO}_2$ considering three air reservoirs: (1) background atmosphere, (2) cave air and (3) soil air (see legend). The average composition of the background atmosphere for the 4 fieldwork sites is indicated by the crosshair. The colored continuous lines indicate the Keeling functions the three-component mixture (atm, cave and soil) and almost it does not differ from the two-component functions (atm-soil and atm-cave); $R^2=0.95$ (Ojo Guareña), $R^2=0.94$ (Castañar), $R^2=0.99$ (Pech Merle). Dotted lines show the 95% confidence intervals for each Keeling function. See text for further data interpretation and discussion.

gas exchange processes are controlled by the upwelling air flow from the zone of fluid-geodynamic influence associated to an active fault with frequent microseisms (Perez-Lopez *et al.*, 2015). The $\delta^{13}\text{C}-\text{CO}_2$ values in air are also consonant with those measured in the CO_2 -rich thermal waters of the aquifer spatially associated to the active fault (between -8.1 and -3.8‰ , according to Ceron *et al.*, 1998). Therefore, degassing from CO_2 -rich groundwater and deep-sourced geothermal CO_2 are the prevailing process responsible of the high abundance of CO_2 and its heavier carbon isotopic composition, which is clearly distinguishable from the epigenetic caves where the isotopically light endmember CO_2 is soil-derived. The upwelling flow of geogenic gases in this cave has a clear influence on the $\delta^{13}\text{C}-\text{CO}_2$ of the soil air above the cave and, to a lesser extent, on the local atmosphere. This effect is noticeable in both the soil air well-mixed with open atmosphere and the soil air mixture with a higher percentage of remaining pure CO_2 produced by respiration in soil (arrows A' and A in Figure 1, respectively). The soil air in Vapor cave sometimes have lower CO_2 values than the other caves, despite the input of geothermal CO_2 . There is an intense upward flux of CO_2 from soil to atmosphere, likely higher than other sites with deeper and wetter soils. Consequently, the soil CO_2 at Vapor cave results from a mixing between atmosphere and the composition of geogenic CO_2 coming from the subterranean atmosphere.

Pending to a full comparative analysis of $\delta^{13}\text{C}-\text{CO}_2$ and other isotopes (D/H for CH_4 and $^3\text{He}/^4\text{He}$) of air samples from Vapor cave, the obtained results ($\delta^{13}\text{C}-\text{CO}_2$ ranging from -4.5 to 7.5‰) indicate that the likely source is a mantle-rooted CO_2 , i.e. a mantle-derived CO_2 flux. Similar carbon isotopic ratios have been described for soil air samples from hydrothermal areas within wider volcanic regions (Wen *et al.*, 2016) and magma-derived CO_2 emissions (Zhang *et al.*, 2016). Other previous studies in hydrothermal sites have describe some wider ranges carbon isotope composition of CO_2 , e.g. from -2.4 to -7.8‰

in submarine hydrothermal vents (Botz *et al.*, 1999) or -1.0 to -9.1‰ in hot springs (Yokoyama *et al.*, 1999). Taking these $\delta^{13}\text{C}-\text{CO}_2$ values as references, the higher $\delta^{13}\text{C}-\text{CO}_2$ may indicate the addition of CO_2 directly from volcanic sources (Mazot *et al.*, 2014) or from underlying sedimentary rocks containing more marine carbonate minerals, i.e. CO_2 is produced mainly by thermal decarbonation (Cinti *et al.*, 2014). On the contrary, the lighter $\delta^{13}\text{C}-\text{CO}_2$ suggest a likely contamination by crustal organic sediments (Zhang *et al.*, 2014).

4. Conclusions

In an attempt to understand the GHGs dynamics in karst systems, we have carried out a pooled analysis of data of abundance and carbon isotopic composition of CO_2 in air from different cave sites with distinctive and opposite environmental conditions. The CO_2 dynamic within the upper vadose zone of karst (accumulation, mixing with background atmosphere or mobilization by diffusion) changes seasonally depending on the air-exchange rate with the external atmosphere, which involves substantial variations on the gas abundances and their carbon isotopic signal. In general, results provide evidence that atmospheric air that is inhaled into dynamically ventilated epigenetic caves (at daily or seasonally scale) can then return to the lower troposphere as CO_2 -enriched air. CO_2 depletion by mixing cave air with background atmosphere prevails during periods and subterranean sites with higher ventilation. On the contrary, when air renewal is hindered the CO_2 of cave air can be mobilized by diffusion to nearby air voids of the vadose zone. In contrast, the first samples obtained in an active hypogenic cave (Vapor cave) exemplify the potential releasing of CO_2 along the faults and in the fractures occurring in the carbonate rocks, which can be an important source in the seismically active areas. The role of subterranean air of karst as sink or source of CO_2 can vary seasonally and it may have a significant influence on the conditions of the adjacent soil and local atmosphere at exterior.

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