



## **Editorial**

# Minerals, crystal structures and geochemistry

# Special Issue dedicated to Peter Williams

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In late 2020, to celebrate Pete Williams' 70th birthday, it was suggested to the editors of *Mineralogical Magazine* to publish a special issue as a tribute to his numerous scientific contributions in crystallography, mineralogy and chemistry. Pete Williams has devoted much of his professional career, both in the laboratory and in the field, to a broad understanding of rare mineral associations. Mineral associations have always been a source of inspiration to him, where one of his goals was to make simple the complexity of the natural environment, whether inorganic or organic. One of his great passions has been unravelling the intricate structure of both natural and synthesised crystals for a diverse range of materials. Pete loves crystallography, mineralogy and chemistry and all his work shows the bridges he built between these fields of science.

## A brief history

Pete Williams was born in Sydney, Australia, in 1950. After finishing high school, he completed a science degree program at Macquarie University (Sydney) majoring in chemistry and earth sciences. Subsequent postgraduate studies there led to the award of a PhD in chemistry.

In 1977 he took up a post-doctoral Research Fellowship working with Prof Bob Gillard at University College in Cardiff, Wales, UK (now Cardiff University), where he then became a Lecturer, Senior Lecturer and finally Reader in Chemistry in 1990. During this period, while coordination chemistry and chiral metal complexes were a main feature of his research, he also began a successful research thrust into low-temperature aqueous geochemistry of particular elements with special reference to the formation of secondary minerals. His well-regarded book *Oxide Zone Geochemistry* published in 1990 is still cited regularly in mineralogical papers (Williams, 1991).

In 1991 he was appointed Foundation Professor of Chemistry in the new University of Western Sydney, joining Prof Pete Leverett (the Foundation Dean of Science & Technology there) a

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fellow Chemist/Geologist/X-ray Crystallographer and with whom he would enjoy a happy teaching and productive research partnership in chemistry, mineralogy and geochemistry for the next 20 years. They became known as 'the two Petes' by their students!

His principal research interests have been in the fields of coordination chemistry, chiral metal complexes, mineralogy, X-ray structure analysis, and supergene geochemistry, and he has been responsible for the publication of more than 350 refereed research articles in these fields. During his career he has successfully supervised a large number of research students leading to over 50 PhD and Masters completions, together with numerous BSc(Hons) completions.

In Australia over the past 25 years he has had an active professional commitment to the fields of mineralogy and geochemistry in general. He has been active as a consultant to the mining industry with respect to exploration and process mineralogy/metallurgy and to industry on various aspects of materials science. This applied work concerned major manufacturing and mining companies, viz: PlatSearch, Birla Mt Gordon, New Guinea Mining, CBH Resources, Nullabor Resources, Golden Cross, Gateway Mining, RGC Thalanga, Silver Standard, Majestic Resources, Australian Resources, Hunt & Hunt, Parsons Brinckerhoff, Newcrest, Eastern Iron, Kimberley Metals and the Queensland and Federal Governments.

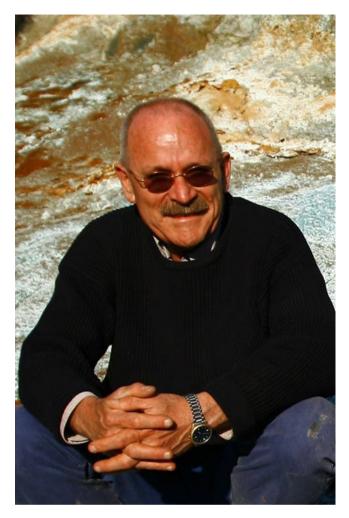
In 2001 he was invited to join the Minerals Advisory Council of Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME), and continued to serve in this role until its closure in 2008.

From 1995 he has served as an Editorial Board Member for the *Journal of the Russell Society*, and the *Journal of Chemical and Engineering Reference Data*. He continues to serve as a Member of the Editorial Board of the Australian Journal of Mineralogy. In addition from 1983–2006 he served as Editor-in-Chief or Co-Editor-in-Chief of the *Journal of Coordination Chemistry*, from 2012–2018 as Principal Editor of the *Mineralogical Magazine* and from 1988–1992 as Co-editor of the *Journal of the Russell Society*. From 2008–2014 he was Chairman of the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification.

In 2003 a new mineral from Johanngeorgenstadt, Saxony, Germany  $[(Ni,Co)_{30}(As_2O_7)_{15},$  translucent, brittle, vitreous crystals with colours that vary from dark violet-red to dark

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**Fig. 1.** Pete Williams on the tailings dump at the Lloyd copper mine, Burraga, New South Wales, Australia in 2004 – the pale blue surface coating is the rare, ephemeral mineral boothite, CuSO<sub>4</sub>·7H<sub>2</sub>O. Pete is a Fellow of the Mineralogical Society of the UK and Ireland; he joined as a member in 1979, and served as Principal Editor of *Mineralogical Magazine* between 2012 and 2018.



Fig. 3. Pete Williams, Emeritus Professor, 2012.

brownish-red, Fig. 2], was named petewilliamsite in recognition of achievements in the field of mineral chemistry ("...for his contributions to mineralogy, both in teaching and research Dr Williams, a geochemist-crystallographer, has made significant contributions to the study of secondary minerals, both in Australia and elsewhere.") (Roberts *et al.*, 2004).

Pete Williams retired as Professor of Chemistry at Western Sydney University in 2012 and was made an Emeritus Professor of the University, a fitting way to honour his achievements (Fig. 3). Pete has made a truly outstanding contribution to teaching and research in Chemistry, and played a significant role in the development and governance of the University. He has been universally admired by the staff he has led and worked with, and by the many students he has taught, mentored and supervised over an extended period of time.

#### Teaching and communicating science

Pete is an excellent communicator of science and teacher who loves spending time in the field. During his time at the University College, Cardiff, UK, he spent several periods in Portugal, mainly at the University of Aveiro, where he was

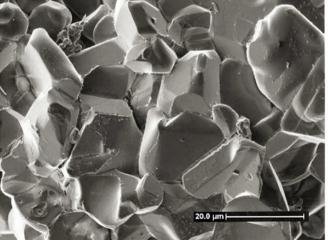




Fig. 2. Left- Scanning electron microscopy image of petewilliamsite (fig. 1 from Roberts et al., 2004). Right – yellow xanthiosite and red/brown petewilliamsite from Johanngeorgenstadt. Rare macro specimen, identified visually, ex. Coll. Larry Conklin. Collection and copyright: Knut Eldjarn, reproduced with permission.

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involved in both research work and teaching thematic seminars. As part of her doctoral work, Pete and Clara Magalhães visited and collected samples from the uranium mines of Urgeiriça, Pinhal do Souto (which had just commenced operations) and Cunha Baixa, as well as some copper mines where copper phosphates were abundant: Miguel Vacas, Mociços and Mostardeira. It was a privilege as all those mines are now closed. Some have become well known for the beautiful mineral specimens that still can be found in mine's tailings.

When Pete returned to Australia in 1991, to take up the Foundation Chair in Chemistry in the recently established Faculty of Science & Technology at the new Western Sydney University, his role was to rapidly develop quality research in Chemistry and to introduce the first PhD and Masters programs in science. He also took the opportunity to introduce a major strand of Geochemistry in the Chemistry degree, where there was an emphasis on fieldwork projects and students could then see "real chemistry in action". The main field sites established by Pete were the Lloyd and Peelwood copper mines near Burraga (80 km S of Bathurst, New South Wales, Australia) and the Sunny Corner silver mine (20 km W of Lithgow, NSW), all being abandoned over 100 years ago but still with significant old workings and remains of the smelters. Here the students learned about the mineralogy, geochemistry, acid mine drainage and mine-site rehabilitation (Fig. 4). They would happily follow Pete around the mine sites, picking up their own specimens of chalcopyrite, malachite, azurite, cuprite, and even native copper, while he explained the important processes of supergene enrichment - the students loved it and Pete was in his element (sic) in some of his favourite places! The field trips led to a variety of research projects and a steady flow of students going on to successful postgraduate studies in Mineralogy and Geochemistry over the next 20 years, and then finding rewarding employment in the mining and mineralsrelated industries which has given Pete so much pleasure.

In addition to classes and seminars, Pete's presentations at international conferences will live long in the memory. Pete gave the plenary lecture during the closing ceremony of the 11th International Symposium on Solubility Phenomena Including Related Equilibrium Processes in Aveiro, Portugal in 2004, with the title "Solutions in the big laboratory: towards a model for metals at the Earth's surface", which ended with a long standing ovation. Once again, the laboratory and the field came together to explain mineral occurrences and chemistry.

#### Contributions to this issue

The authors of the contributions to this issue are Pete's friends and former students. Although some friends and colleagues with whom he worked most closely have unfortunately disappeared, many contributed to this issue. The scientific topics of this special issue show the variety of Pete's scientific interests. The works presented are divided into the generic thematic areas of crystallography, mineralogy, nomenclature, geochemistry and archaeology/building conservation, which are the areas where Pete had an active professional commitment and a significant publications list.

The first article in this special issue devoted to Pete, 'Reaphookhillite, MgZn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, the Mg analogue of parahopeite from Reaphook Hill, South Australia' by Peter Elliott describes a new phosphate mineral from a mine famous for unusual mineral associations, described and studied in the past

by Pete Williams. This article presents a picture of a thin tabular crystal of colourless and transparent reaphookhillite (0.3 mm wide) formed as an overgrowth on a parahopeite crystal (Elliot, 2022). Papers by Anthony R. Kampf, Mark A. Cooper, Aaron J. Celestian, Chi Ma and Joe Marty 'Dendoraite-(NH<sub>4</sub>), a new phosphate-oxalate mineral related to thebaite-(NH<sub>4</sub>) from the Rowley mine, Arizona, USA' and 'Relianceite-(K), a new phosphate-oxalate mineral related to davidbrownite-(NH<sub>4</sub>) from the Rowley mine, Arizona, USA' also describe new phosphate mineral species [dendoraite-(NH<sub>4</sub>), (NH<sub>4</sub>)<sub>2</sub>NaAl(C<sub>2</sub>O<sub>4</sub>)(PO<sub>3</sub>OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and relianceite-(K),  $K_4Mg(V^{4+}O)_2(C_2O_4)(PO_3OH)_4(H_2O)_{10}$ and list the minerals associated with them (Kampf et al., 2022a, 2022b). Both articles present images of sprays of each mineral. One more secondary phosphate, kintoreite [ideally PbFe<sub>3</sub>(PO<sub>4</sub>) (PO<sub>3</sub>OH)(OH)<sub>6</sub>], from the Tripi mine, Alì, Peloritani Mountains, Sicily, Italy, is described by Daniela Mauro, Cristian Biagioni and Federica Zaccarini, in the article 'A contribution to the mineralogy of Sicily, Italy - Kintoreite from the Tripi mine, Peloritani Mountains: occurrence and crystal structure'. This mineral with origins related to the weathering of primary ores, is suggested by the authors, "as a potential host for lead", which together with other lead containing minerals, such as pyromorphite, could play a role in controlling the geochemical behaviour of this element (Mauro et al., 2022).

The work 'Calciolangbeinite-O, a natural orthorhombic modification of K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and the langbeinite-calciolangbeinite solid-solution system' by Igor V. Pekov, Natalia V. Zubkova, Irina O. Galuskina, Joachim Kusz, Natalia N. Koshlyakova, Evgeny V. Galuskin, Dmitry I. Belakovskiy, Maria O. Bulakh, Marina F. Vigasina, Nikita V. Chukanov, Sergey N. Britvin, Evgeny G. Sidorov, Yevgeny Vapnik and Dmitry Yu. Pushcharovsky describes the first natural orthorhombic langbeinite-like sulfate. The samples studied by the authors represent the whole compositional range of the langbeinite-calciolangbeinite solid-solution, which is not very common. Pictures show colourless to white calciolangbeinite-O overgrowing sanidine and crystallised together with hematite and iron-black tenorite. Many other minerals are also described from the localities where the samples analysed were collected (Pekov et al., 2022). Another sulfate mineral [CaCe<sub>2</sub>Cu<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH)<sub>12</sub>·8H<sub>2</sub>O] is described by Mike S. Rumsey, Frank C. Hawthorne, John Spratt, Jens Najorka and Wren Montgomery in the article 'Bridgesite-(Ce), a new rare-earth element sulfate, with a unique crystal structure, from Tynebottom Mine, Cumbria, United Kingdom'. Translucent acicular blue crystals are associated and often intergrown mainly with brochantite, malachite, serpierite, devilline, gypsum, aragonite, jarosite, pyrite, lanthanite-(Ce) and undifferentiated iron hydroxide/oxides (Rumsey et al., 2022).

'Sluzhenikinite,  $Pd_{15}(Sb_{7-x}Sn_x)$   $3 \le x \le 4$ , a new platinum group mineral (PGM) from the Oktyabrsk deposit, the Noril'sk deposits, Russia' by Anna Vymazalová, Mark D. Welch, František Laufek, Vladimir V. Kozlov, Chris J. Stanley and Jakub Plášil describes the physical properties, chemical composition, crystallographic parameters and the structure of a new palladium mineral discovered in the pegmatitic galena–chalcopyrite massive ore from the Oktyabrsk mine. Reflected-light and back-scattered electron images show associations of sluzhenikinite with sperrylite, cubanite, insizwaite, sobolevskite, stibiopalladinite galena, chalcopyrite and bornite (Vymazalová *et al.*, 2022).

Martin Ondrejka, Alexandra Molnárová, Marián Putiš, Peter Bačík, Pavel Uher, Bronislava Voleková, Stalislava Milovská, Tomáš Mikuš and Libor Pukančík in the article 'Hellandite522 M. Clara F. Magalhães *et al*.



Fig. 4. Photo of the two Petes in 2008 with final-year geochemistry students at the Sunny Corner silver mine site, New South Wales – note barren landscape and old smelter chimney.

(Y)-hingganite-(Y)-fluorapatite retrograde coronae: a novel type of fluid-induced dissolution-reprecipitation breakdown of xenotime-(Y) in the metagranites of Fabova Hol'a, Western Carpathians, Slovakia' analyse the formation of secondary coronae, containing crystals of hellandite-(Y)  $[(Ca,REE)_4Y_2Al_2(B_4Si_4O_{22})(OH)_2]$  and hingganite-(Y)  $[Y_2Be_2Si_2O_8(OH)_2]$ , that developed around rare-earth element (REE) phosphates in metagranitic rocks, resulting from the activity of external origin fluids probably from adjacent magmatic, metamorphic or sedimentary rocks (Ondrejka et al., 2022).

The next three papers describe secondary minerals associations from three different locations and geological settings in Australia. Dermot A. Henry and William D. Birch in the article 'The Wombat Hole Prospect, Benambra, Victoria, Australia: a Cu-Bi-(Te) exoskarn with unusual supergene mineralogy' analyse the complex array of unusual secondary copper and bismuth bearing minerals. They conclude that "the small extent of the skarn and its remote setting, where contact relationships are obscured, lead to some uncertainty about the paragenesis of the secondary mineralogy" (Henry and Birch, 2022). Ian T. Graham, Adam McKinnon, Angela Lay, Karen Privat, Khalid Schellen, Lachlan Burrows, Elizabeth Liepal and Hongyan Quan in their article 'Gold and aurostibite from the metaturbiditehosted Au-Zn-Pb-Ag Hera deposit, southern Cobar Basin, central NSW, Australia: geochemical and textural evidence for gold remobilisation' describe the mineral associations, textures and chemistry of gold, electrum and aurostibite from associations

within the Hera deposit (Graham et al., 2022). A rich and complex association of gold with galena, sphalerite, chalcopyrite, pyrrhotite, gudmundite, tetrahedrite and aurostibite was found and they conclude: "The wide range in gold compositions and associations is attributed to widespread physical and chemical remobilisation associated with multiple periods of deformation, principally in the form of shear zones and faults". Erik B. Melchiorre is the author of 'Stable isotope and geochemical evidence for genesis of secondary copper deposits at Girilambone, New South Wales, Australia' where he analysed the conditions of formation, in the oxidation zone, of wellcrystallised malachite dominant near the surface, and azurite, which dominates in deeper zones. Oxygen isotope thermometry estimates mineral formation temperatures, and isotopic carbon fractionation, which is ideal for identifying carbon sources, is consistent with isotopically light bacterial carbon and/or atmospheric carbon sources. Atacamite-group minerals crystalise as a consequence of modern Girilambone operations (Melchiore, 2022).

'Isotopic exchange of oxygen, sulfur, hydrogen and copper between aqueous phase and the copper minerals brochantite, libethenite and olivenite' by Juraj Majzlan, Ryan Mathur, Rastislav Milovsky and Stanislava Milovská presents the fractionation factor determined for the isotopes of oxygen, hydrogen, sulfur or carbon for the aforementioned minerals and their corresponding aqueous solutions, at temperatures between 30 and 70°C (Majzlan *et al.*, 2022). D. Kirk Nordstrom, in 'Evaluation for internal consistency in the

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thermodynamic network involving fluorite, cryolite, and villiaumite solubilities and aqueous species, at 25°C and 1 bar', evaluates the published values of thermodynamic quantities, for their internal consistency, and calculates reliable values for the solubility constants and Gibbs energy of the solubility reactions of fluorite (CaF<sub>2</sub>), cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and villiaumite (NaF) (Nordstrom, 2022).

In their paper Fabrice Dal Bo, Henrik Friis and Stuart J. Mills have established the 'Nomenclature of wöhlerite-group minerals'. The general formula of minerals belonging to this group is given by  $X_8(\mathrm{Si_2O_7})_2W_4$ , where  $X=\mathrm{Na^+}$ ,  $\mathrm{Ca^{2+}}$ ,  $\mathrm{Mn^{2+}}$ ,  $\mathrm{Ti^{4+}}$ ,  $\mathrm{Zr^{4+}}$  and  $\mathrm{Nb^{5+}}$ ; and  $W=\mathrm{F^-}$  and  $\mathrm{O^{2-}}$  incorporating significant amounts of other elements. The minerals of the wöhlerite-group crystallise in different unit-cell settings and symmetries, depending on the cationic ordering in the octahedral walls and the relative position of the disilicate groups. The schematic and idealised representation of the cationic distribution in the walls of the minerals belonging to this group is presented (Dal Bo *et al.*, 2022).

The last three articles address topics very dear to Pete, e.g. the analysis of the composition and association of minerals in ancient artefacts. In these three diverse papers, there is a common denominator - at least one of the members of each team worked for several years with Pete Williams. This influence shows by the presence of Pete's fingerprint, evident in the intersection of views of different scientific areas, opening doors to new investigations. Ruiliang Liu and A. Mark Pollard in their article 'Asking different questions: highly radiogenic lead, mixing and recycling of metal and social status in the Chinese Bronze Age', pose several questions, raised by the lead isotopic analysis in bronze objects from the Chinese Shang dynasty [ca. 1600 -1045 BCE (before common or current era)]. Questions that go beyond mere geochemical and geological interpretations about the origin of raw materials and that have thrown new light on questions from archaeological narrative, such as "which important resources were managed by consumers of different social status within early dynastic China" (Liu and Pollard, 2022). Richard E. Bevins, Nick J. G. Pearce, Rob A. Ixer, Stephen Hillier, Duncan Pirrie and Peter Turner in their article 'Linking derived debitage to the Stonehenge Altar Stone using portable X-ray fluorescence analysis' look for the origin of the Stonehenge Altar Stone. Non destructive XRF of the Altar Stone combined with analysis of of fragments that were only presumed to be from the Altar Stone, showed an identity between the two, meaning the more accesible fragments could be used as proxies to characterise potential source material. However, the presence of baryte in appreciable amounts in both materials raises the possibility that the Altar Stone does not come from the Old Red Sandstone sequences of Wales. The authors conclude that the presence of baryte could help in the search for the source of the Stonehenge Altar Stone (Bevins et al., 2022). The final article, by Alice Tavares, M. Clara F. Magalhães, Rosário Soares and Aníbal Costa, on 'Characterisation of salts progression in walls of earthen architecture heritage' combines the information obtained from laboratory tests with those carried out in situ in a house containing two types of earthen construction - adobe masonry walls and formed masonry walls - to characterise the conditions for the appearance and phase transition of thénardite (Na2SO4) and mirabilite (Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O), and determine how to prevent progression of salt effects in the two types of earthen construction, to support future recommendations for building conservation, based on the identification of environmental conditions relevant to their occurrence (Tavares et al., 2022).

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