# "R.W. Boyle's History of Geochemistry, Part I: from Antiquity to Medieval Times"

*by*
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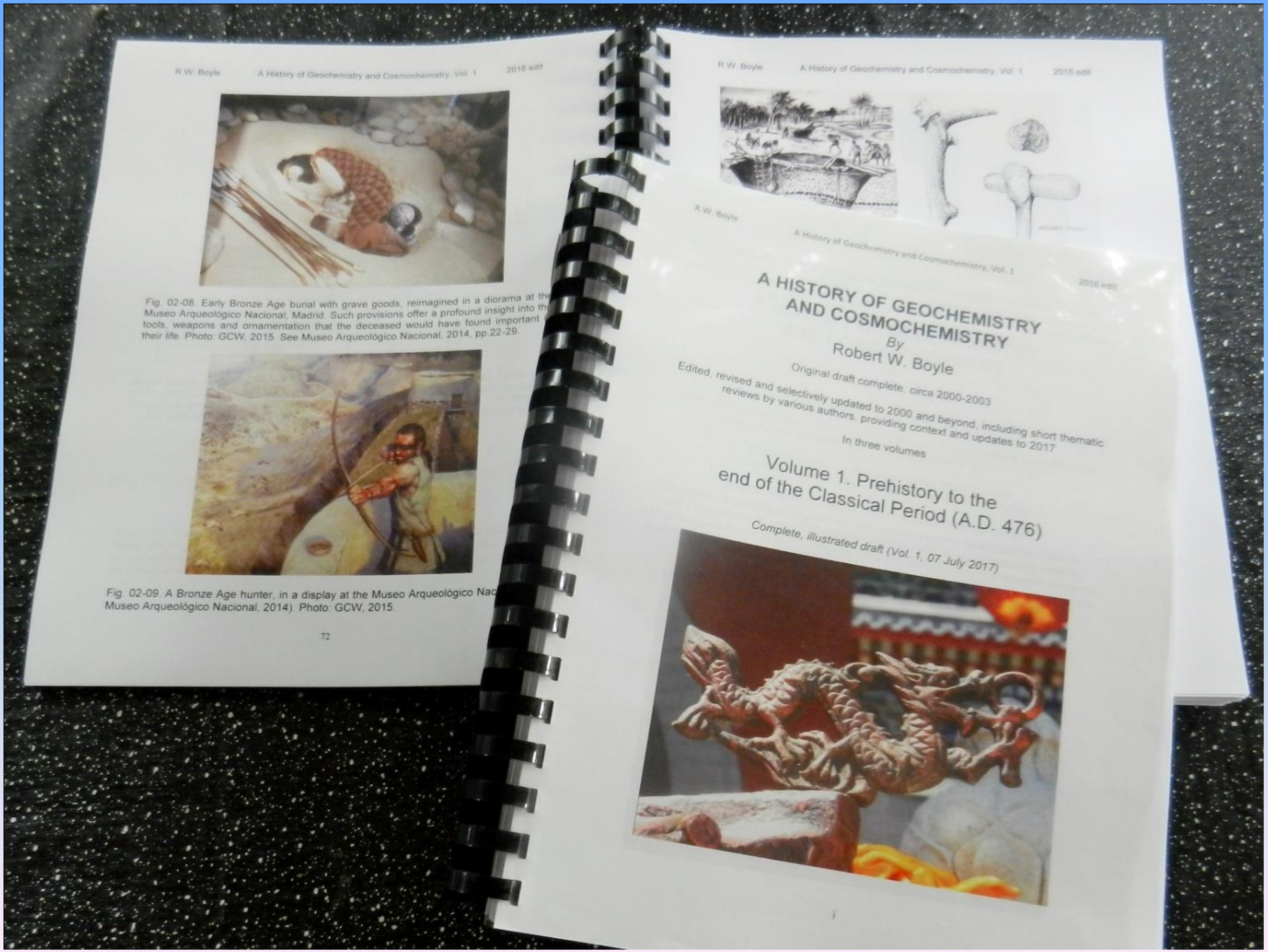
# A brief history of the History

- Robert William Boyle (1920-2003) was a geologist and geochemist, whose long career included a stint at the Geological Survey of Canada (1952-1985).
- He published many significant papers and monographs, most famously on gold and silver deposits, but also on uranium and thorium, base metals, and on the use of indicator elements (such as As and Sb) in geochemical prospecting.
- The prospect of retirement was evidently not his idea of fun: the great work of the last 18-20 years of his life was a new work, a synthesis of a lifetime of research:

“A History of Geochemistry and Cosmochemistry” …

# The "metahistory" is continued later. Let's get started on the Real Thing…



# Human origins and the rise of "tech"

| Region | Palaeolithic | Mesolithic | Neolithic |
| --- | --- | --- | --- |
| Dates BP (Before the Present, nominally "Present" = 1950 A.D.) | | | |
| North Africa, Middle East & Asia | **Lower**: 2,500,000 to (800,000 to) 120,000. **Middle**: 120,000 to (100,000 to) 30,000. **Upper**: 30,000 to 12,000 | 10,000 to 7,000 | 7,000 to 6,000 (Middle East) or 4,500 (China) |
| Europe | | | To 5,000 or 3,800 |
| N.America | | | To 500 |
| Australia | | | To 300 |

# Time Passages

| Period | Date (B.P.) | Notes |
|---|---|---|
| Iron Age | Begins 3,200 | |
| Bronze Age | 5,500-3,200 | True bronze (Cu + Sn ± As…) replaces Cu *circa* 5,000 |
| Chalcolithic | 7,500-5,500 | Native Cu employed in N.America by 7,000 |
| Neolithic | 8,000-5,500 | Crops and animals domesticated: |
| | 7,000 | Africa |
| | 7,200 | Americas |
| Mesolithic | 12,000-8,000 | |
| | 9,500 | China, India, Japan, Korea |
| | 11,000 | Wheat in Middle East |
| | 11,400 | Figs in Jordan |
| | 12,000-10,000 | Cultivation of wild plants |
| | 12,000 | Stone tools in Britain date to 700,000, but current Brits arrived between end of last glaciation (12,000) to inundation of Doggerland (8,000) |
| Late Palaeolithic | 30,000-12,000 | Homo florensis d. 18,000 |
| | | Homo neanderthalensis d. 23,000 |
| Middle Palaeolithic | 120,000- 30,000 | Homo heidelbergensis, 600,000 |
| Lower Palaeolithic | 2,500,000-120,000 | Homo ergaster, 1,500,000 |
| | | First use of fire, 1,500,000 |

# What's in a word? – geo(al)chemistry

- *Chemistry* was not in general use prior to the 6th century A.D.
- *Chemia* appeared around 300 A.D. in the works of Zosimos of Panopolis, an alchemist in southern Egypt.
- *Al* (Arabic for "the") + *chemia* = *alchemia*
- Various Arabic, Egyptian and Hebrew roots have been proposed for Chemistry
- Plutarch suggested the root is *khem*, meaning the black land (soil) of the Nile, hence the Egyptian art…
- Boyle explores the origins and speciation of *geochemistry* in detail (as per the five *spheres*), whence: *lithogeochemistry, pedogeochemistry, hydrogeochemistry, atmogeochemistry, biogeochemistry*, and applications such as *cosmochemistry, exploration geochemistry, environmental geochemistry*….

# Origins – useful stones, e.g., Flint, Obsidian and Ochre (pigments)

- Early items – flint (and other varieties of chert) for sharp edges and points, and pigment like Fe oxides in caves from Europe to Tasmania.


Above: English flint transformed to spear point by expert knapper Reuben LeBaron.

Right: siliceous volcanic glass (obsidian) from China, showing conchoidal fracture like flint.

# Origins: Fire and Iron, from the Skies

- Early **glass**, courtesy of impact events – **Darwin glass** was used for sharp tools in Tasmania, *circa* 15,000 B.C., harvested from a 700,000 BP impact structure and traded >100 km.

- **Iron meteorites** – Ni-Fe beads with relict Widmanstatten pattern and taenite (Ni-rich variety of native Fe) found in Egypt, 3,300 B.C. Smelting not required. Later use of iron by the original settlers of Greenland (the Cape York iron).

Right: a dagger from the burial shroud of Tutankhamen, late $18^{th}$ Dynasty, *circa* 1325 B.C. [BBC, 2016]

# Gebel Kamil, southwest Egypt

- A crater with >1 tonne of meteorite "shrapnel" found in the desert of southwest Egypt, the Gebel Kamil iron meteorite is one possible source of small amounts of natural iron used in Pharaonic Egypt.

Right: a 2.5-kg angular shard of the Gebel Kamil iron meteorite, which contains 19.8 wt.% nickel. This material is geochemically distinct from any terrestrial iron ores, including the rare native iron, found in some basaltic intrusions in Greenland and Russia.

# Origins… shiny stones (native elements)

Above: native iron in basalt from the Putorana plateau, Russia. Such iron contains modest Ni (*circa* 2 wt.%) unlike most meteoritic iron alloys.

Boyle wrote several articles on native elements, of which a very few are widespread, such as Au, Ag and Cu. Below: an indication from the MINLIB database of the number of citations for each element. 2017 version (there are now actually 30-plus native elements known, though many are vanishingly rare).

| *Native element* | *No. of records* |
|---|---:|
| Native cadmium, Cd | 2 |
| Native zinc, Zn | 4 |
| Native tin, Sn | 11 |
| Native lead, Pb | 36 |
| Native mercury, Hg | 41 |
| Native osmium, Os | 45 |
| Native tellurium, Te | 73 |
| Native arsenic, As | 78 |
| Native iron, Fe | 103 |
| Native platinum, Pt | 114 |
| Native sulphur, S | 192 |
| Native bismuth, Bi | 254 |
| Native silver, Ag | 542 |
| Native copper, Cu | 684 |
| Native gold, Au | 1739 |

# Native copper

- Native copper is unique amongst the native elements in forming locally-abundant, and sometimes very large (kg to 100-tonne scales) masses, that can be cold-worked.



Copper (both native and as its many other ore minerals) may be found by colourful showings of secondary minerals (above: Mineral de Pozos, Mexico). The Keweenaw peninsula of Michigan is noted for masses of native Cu, which were known and worked by native peoples at least 7,000 BP.

# Tin: Cassiterite and Bronze



Some early mining districts in Turkey and Iran, amongst the earliest of major mining and metal industries --- other early sites have been excavated in China, India, Armenia and Israel (etc).

Above: cassiterite, $SnO_2$ -- the principal ore mineral of tin.
Old Beam mine, Bugle, Cornwall,

# Rise of the metallurgists!

- *Geochemistry* and *metallurgy* both reflect the realities of *mineralogy* … certain elements are associated one with the other, e.g., chalcophile or siderophile associations. This knowledge evolved, via alchemy, into modern chemistry.

Early dates of mining / working / refining metals include:

**Hg** – known long ago as cinnabar, HgS
**Cu** – cold-worked native Cu, in Turkey (7,000 B.C.), Baluchistan (6,000 B.C.), and Minnesota, *circa* 5,000 B.C.
**Meteoritic Fe** – Iraq, 5,000 B.C.
**Bronze** (Cu +Sn / As-Sb-Pb), 3,500 B.C.
**Major Cu & bronze working**, Turkey & China, *circa* 2,000 B.C.
**Smelted Fe** – various, *circa* 3,000-2,000 B.C.
**Brass** (Cu + Zn), India, 1,600 B.C.
**Sn** – Egypt, 1,500 B.C.

Top-base: Cu / Au / Sn

Top-base: Fe / Hg / Zn

# Cinnabar, mercury

Above: sample of cinnabar (with metacinnabar plus minor pyrite and stibnite) from the famed Almaden mine, Spain. Theophrastus, and contemporary Chinese, Indian and western alchemists and scholars, were familiar with cinnabar and mercury. Almaden was one of several ancient sources mentioned by Pliny the Elder. HgS yields Hg plus $SO_2$ with gentle roasting at 357°C. It boils out of the sample and is easily condensed.

# Review: key raw materials

Perhaps 3 dozen mineral species were generally known in Ancient times. These included some native elements. Boyle's Chapter 3 has been split into six parts for ease of digestion. 29 elements and classes of materials are dealt with (Table, and a few examples in the following slides)… Note that not all were known as elements, e.g., aluminium was encountered as clay and alum.

| **Gold** | **Silver** | **Copper** | **Tin** |
|---|---|---|---|
| **Lead** | Zinc | Cadmium | Mercury |
| **Iron** | Nickel | Cobalt | Platinum |
| Antimony | Arsenic | Bismuth | Tungsten |
| Molybdenum | Uranium | **Phosphorus** | Manganese |
| Boron | Aluminium | Tellurium | **Sulphur** |
| **Carbon** | **Gemstones and allied materials** | **Pigments** | **Industrial minerals** |
| **Organic substances and products** | | | |

# Gold

Gold is a rare but widespread native metal, found in both lode and placer deposits. Boyle wrote three books on gold, starting with a memoir on the Yellowknife camp (1961).

Above: touchstones for visual assay of gold alloys.
Above right: stone stamp used for gold disc production, Waterford, Ireland, *circa* 2,000 B.C.
Right: modern placer gold from northwest Guyana.

# Lead and Zinc



Early, recognizable ore minerals of lead included minium (above, from Colorado) and galena (above right, Peru).

Iberia was the largest producer of lead in the Roman world. The metal was smelted on site, made into hefty (33.5-kg) ingots (right), and shipped to Rome for manufacturing purposes.
Specimens on display in Madrid.

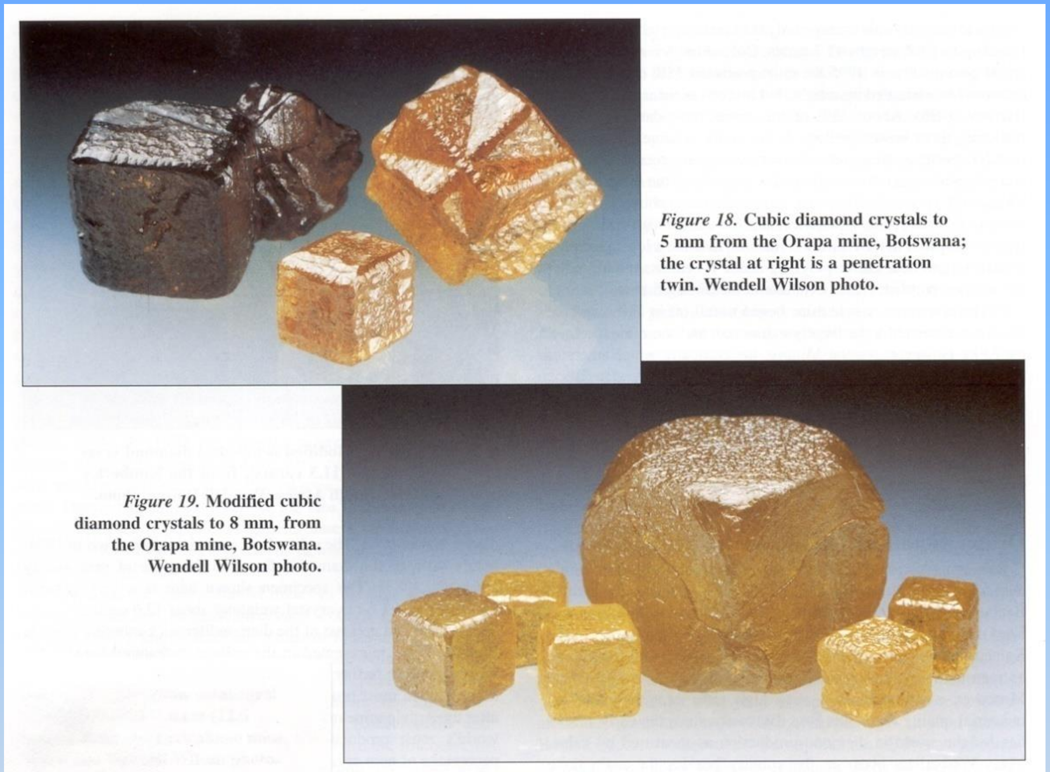
# Hot springs, sulphur

Sulphur (above: southern Spain), like carbon (graphite, diamond, amorphous carbon) is readily identified, and found in particular in salt domes and in active volcanic and geothermal systems (right: New Zealand).

# Arsenic, antimony

Boyle's modern work included studies of uses of chalcophile minor elements such as arsenic and antimony in mineral exploration. They form their own minerals, such as stibnite ($Sb_2S_3$ – from Romania, above right), and are also enriched in some geothermal systems, such as the Champagne Pool, North Island, New Zealand (above and previous slide).

# Carbon: graphite to diamond



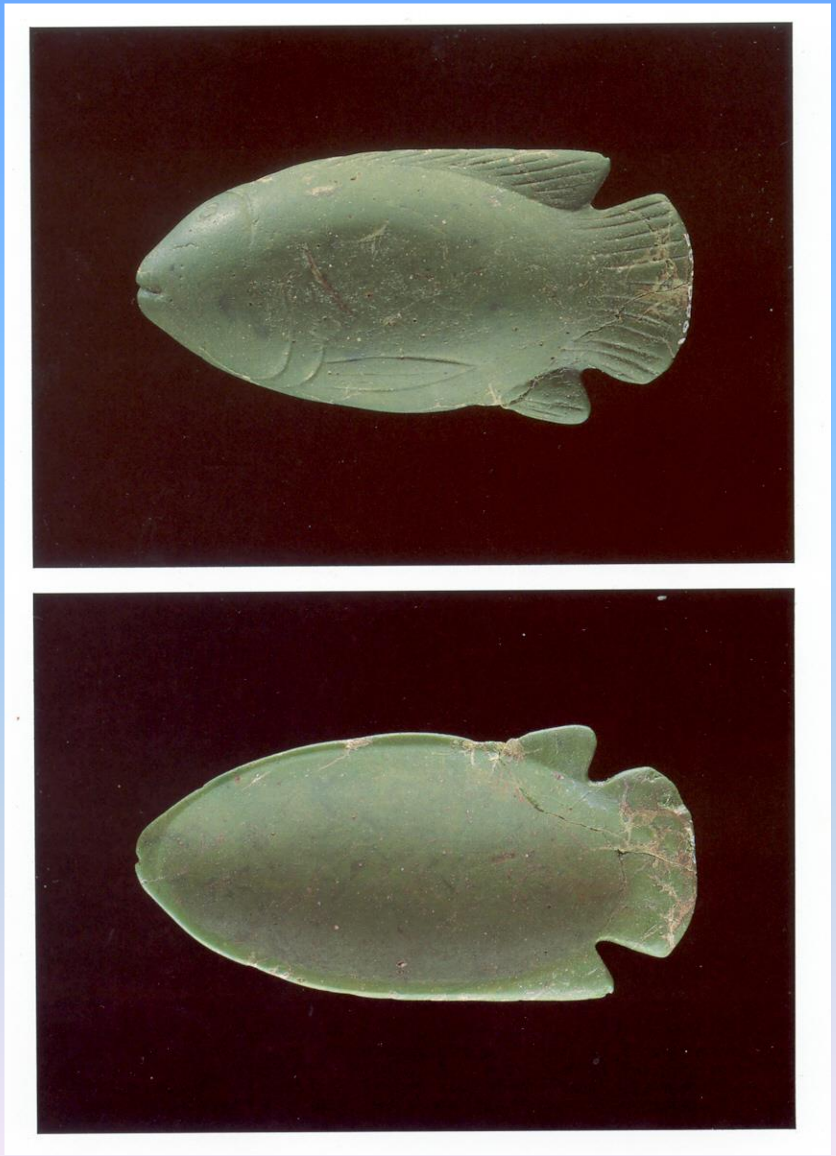

Above left: graphite with diopside, Tanzania. Graphite was known long ago in places such as Egypt and Sri Lanka.

Above right: fine crystals of diamond from Orapa, Botswana (images from *Mineralogical Record*). Diamond was first known in India, perhaps as long ago as 1200 B.C.

# Jade

Durable and often of great beauty, jade has been used worldwide since ancient times. Right: Zapotec jade, and the Monte Alban site in Oaxaca (Mexico). Centre left: a jade *bi* from China. Below: jadeitite sourced to seasonal mountain quarries in northwest Italy, found as high-status, ceremonial axeheads in Ireland, *circa* 4,000 B.C.

# Glass



Above: glass weights from Islamic Egypt, 7th to 12th centuries A.D. Right: a dish of green glass from the late 18th Dynasty of ancient Egypt, circa 1400-1300 B.C.  Minerals such as natron (hydrous sodium carbonate) lower the temperature of fusion, and can be used in glaze. Glass manufacture may have begun in Mesopotamia, and soon spread to Egypt.

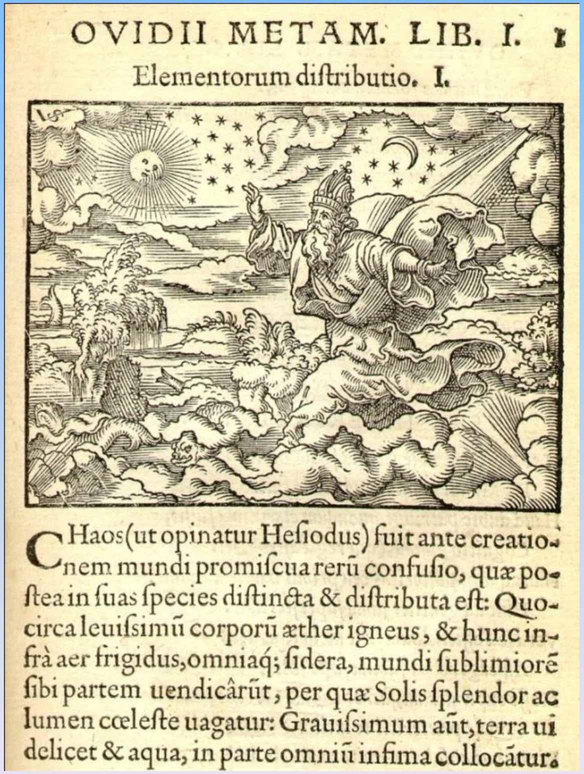
# Other substances

Near the end of the sprawling chapter 3 (metals and materials), Boyle allots 10 pages to early explorations of sundry organic substances and products, including beer!

Early examples include urine (whence, much later, phosphorus and urea); wine and beer; vinegar; organic dyes; cooking and baking products; paper and ink. There is some good chemistry in all of these!

# The European classical period

- Many are the Greek and Roman writers and philosophers discussed in Boyle's review. These include Democritus (460-370 B.C.), Plato (427-347 B.C.), Aristotle (384-322 B.C.), Theophrastus (371-288 B.C.), Ovid (43 B.C.-18 A.D.) and Pliny the Elder (23-79 A.D.).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Elementorum diſtributio. I.

CHaos (ut opinatur Heſiodus) fuit ante creationem mundi promiſcua rerũ confuſio, quæ poſtea in ſuas ſpecies diſtincta & diſtributa eſt: Quocirca leuiſsimũ corporũ æther igneus, & hunc infrà aer frigidus, omniaq; ſidera, mundi ſublimiorẽ ſibi partem uendicârũt, per quæ Solis ſplendor ac lumen cœleſte uagatur: Grauiſsimum aũt, terra uidelicet & aqua, in parte omniũ infima collocâtur.

Woodcut based on Ovid's Metamorphoses.

Another later image: the death of Pliny the Elder.

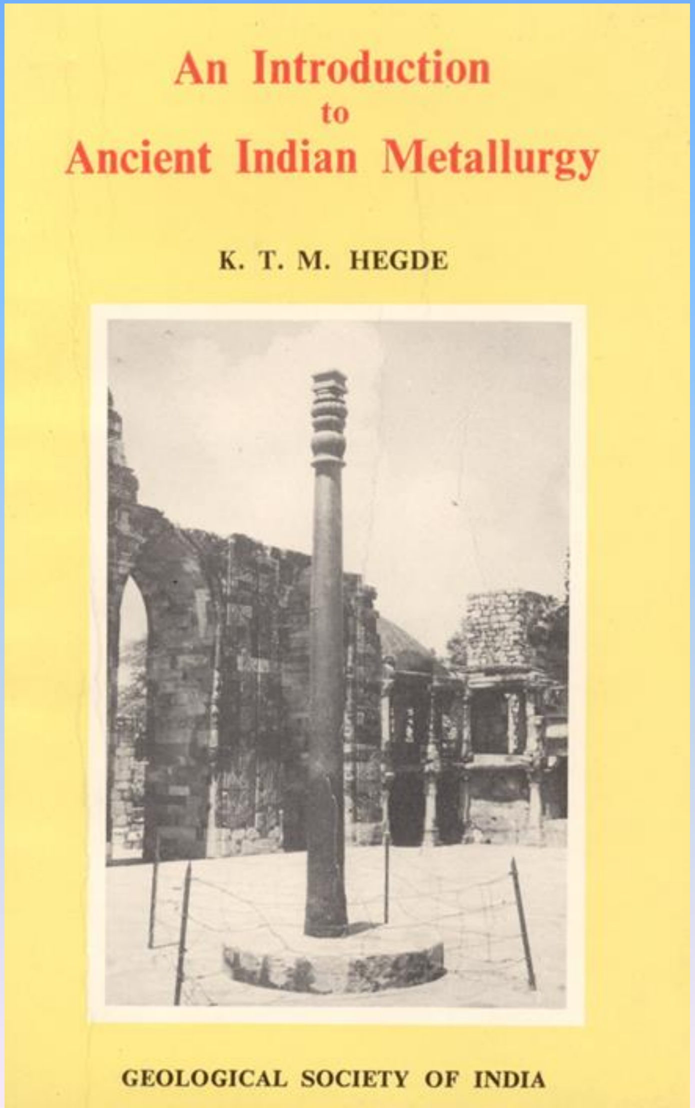
# China



Boyle has much to say of China in Volume 1, often quoting the matchless sinophile scientist Joseph Needham. Above: map from Cunliffe, showing maximum extent of the Shang dynasty (1600-1046 B.C.). Top left: a massive bronze *ding* of Shang vintage Lower left: a model of Zhang Heng's seismoscope of 132 A.D.

# India

- As with China, the history of ancient India is much-studied.
- The Sanskrit Vedas, dating to at least 1200 B.C., are one source of ideas on the nature of matter.
- An equivalent to Theophrastus' "On Stones" is the Arthashastra of Kautilya, written in the 4th century B.C. He talks of mines and metals, gemstones, and the uses of gold and silver.




The iconic Iron Pillar of Delhi, a corrosion-resistant wonder that is some 1600 years old, a product of forge welding. The much-studied landmark weighs over 6.5 tonnes.

# The Medieval Period

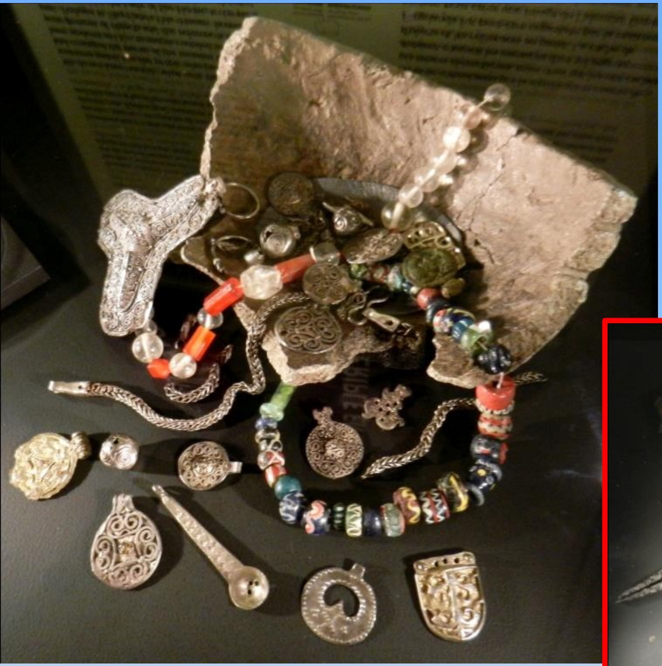
- Some would define this as the time from the fall of Rome in the west (476 A.D.) to the fall of Constantinople in the east (1453 A.D.). Forces at play include the Church and monarchies in Europe, and the growing influence of Islam, whose scholars, in the Middle East and Egypt, and to the west in Moorish Spain, preserved, translated and ultimately propagated some of the classical works that might otherwise have been lost. The rise of universities, first in northern Italy and Paris, and later in England, Germany and elsewhere, provided counterpoints to the Church, and centres for studies both abstruse and, eventually, practical in nature.

# A New Wave of Thought

A “House of Wisdom” at Baghdad was established by an Abbasid caliph, one of a number of new centres of learning.

Amongst the stars of the new centres of learning were Geber, Rhases, Avicenna, al Biruni and Averroes.

# Medieval crafts and use of materials



Above and centre: Viking use of stone and metal in jewellery, and iron-working tools and slag.
Right: the Crown of Reccesvinth, with sapphires and pearls. From the Visigoths of Spain, in the 7th century.

# Sources

- A cast of hundreds, and indeed thousands! Volume 1 quotes Biblical and other ancient sources. The total in the extended Boyle database is currently *circa* 3,200 references (602 quoted so far, in Vol. 1). Some modern works that post-date the original draft are:


- **Cunliffe, B., 2015.** By Steppe, Desert, and Ocean: the Birth of Eurasia. Oxford University Press, 530pp.
- **Garrett, R.G., 2004.** Robert William Boyle - a tribute: 3 June 1920-5 August 2003. Geochemistry: Exploration, Environment, Analysis, v. 4, p. 3-5.
- **Mithen, S., 2004.** After the Ice: a Global Human History, 20,000-5,000 B.C. Harvard University Press, 622pp.
- **Winchester, S., 2008.** The Man who Loved China: the Fantastic Story of the Eccentric Scientist who Unlocked the Mysteries of the Middle Kingdom. Harper, 328pp. (*biography of Joseph Needham*).

# Acknowledgements


- Heather Robinson
- The technical experts / fellow editors on the patient team (Charles Butt; Bob Garrett; Ray Lett; Rob Bowell; Fiona Eddison)
- Jim Laidlaw (who actually volunteered to read vol. 1!)
- William Thurgood for notes on tin in ancient Cornwall
- AAG for entrusting the project to us.

# Conclusion – the Story So Far

- The Prehistoric and western Classical periods (Volume 1), ending at 476 A.D., saw huge advances in both technological uses and the scientific / philosophical understanding of numerous metals, other elements and minerals.
- The "Dark Ages" were not always dark, everywhere and all the time, and by the end of the Medieval period (which some define as the fall of the eastern Roman empire in 1453) much of the older knowledge had been rescued within the Islamic world and universities were rising in Europe. Remarkable advances had also been made elsewhere, particularly in China and the Indian subcontinent.

- 1500 on?
- We are still at work on volume 2, with parts of the 19th century edited and illustrated. If you have time for five more slides, we can outline how the *ur*Boyle (2003) is structured now, and how it is progressing.

# “A History of Geochemistry and Cosmochemistry”

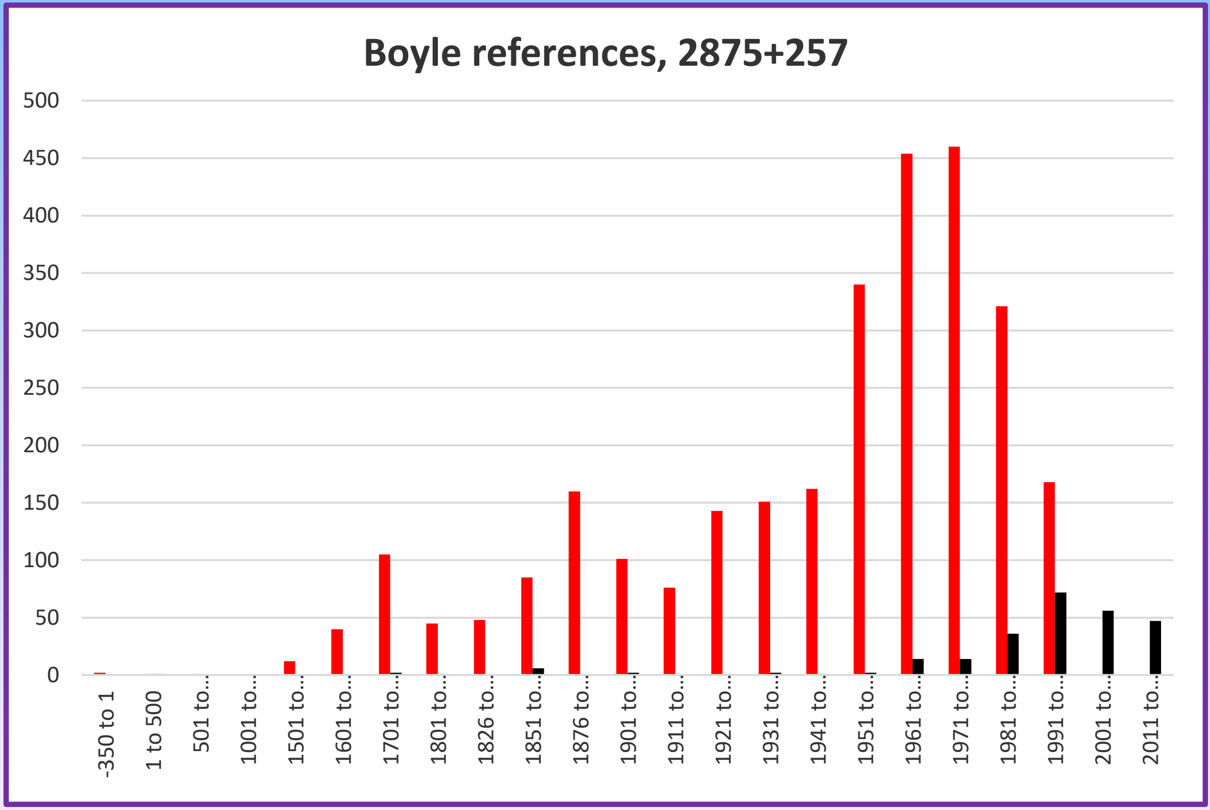
- Stage 1. The writing. Boyle assembled his magnum opus with care, visiting many libraries and consulting many sources. The draft was finished just before he passed away, in 2003.
- Stage 2. The “feasibility study”. Not surprisingly, colleagues at the Association of Applied (formerly, Exploration) Geochemists (AAG) were interested in the work. Charles Butt (CSIRO) read the text and made numerous edits and suggestions. Bob Garrett (GSC) made additional; comments and suggestions. At this point, the text occupied 1,651 double-spaced pages, not counting some 2,875 references (another 176 pages). There was <u>no</u> illustration. The text slumbered on…

# "A History of Geochemistry and Cosmochemistry"

- Stage 3. Editing, restructuring, illustrating and updating. Graham Wilson heard of the dormant project in 2015. AAG honoured him with a bound hard copy and files for what seems to be close to 100% of the intended text. Encouraged by Boyle's daughter, Prof. Heather Robinson, and a small group of interested souls (Butt and Garrett included), GCW went to work, and Volume 1 of the putative *trilogy* was ready in two years, a manuscript totalling some 750 pages, with 100-plus figures, plus tables, a special version of the periodic table, and some 600 references, which are now distributed amongst the various chapters and sub-chapters for ease of use.

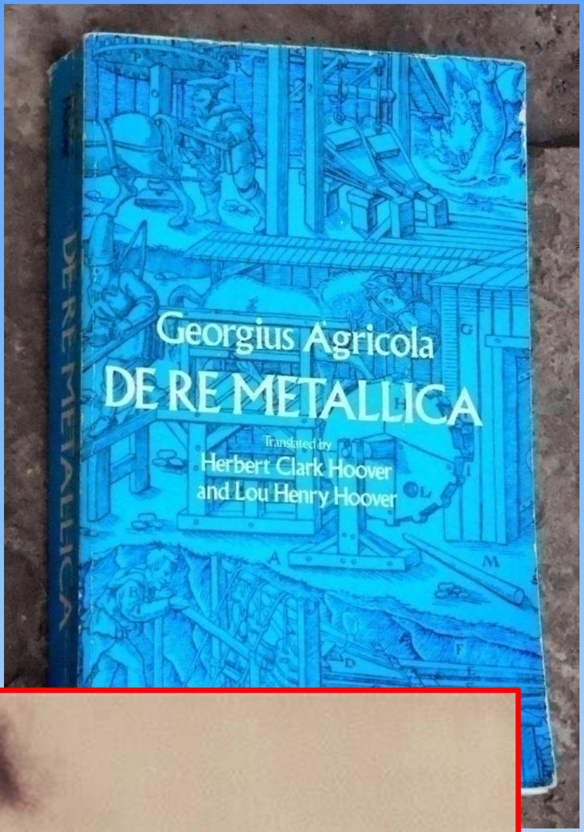
# Sources (so far)

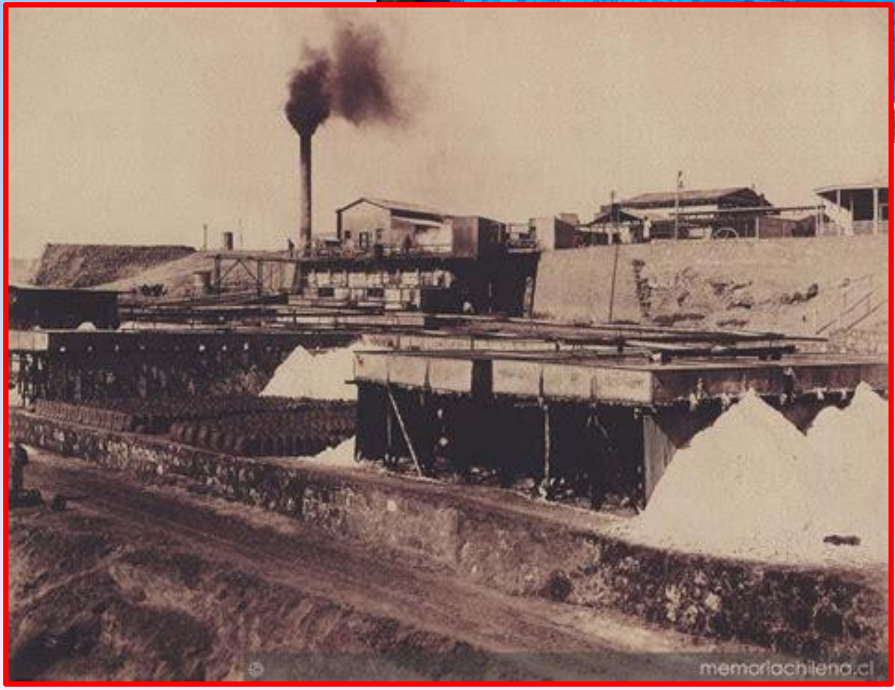
- Boyle's manuscript ended with an A-Z bibliography of 2,875 references. No-one knows, yet, whether he cited all of these in the 3 volumes. The text was imported into the ancient but reliable Q&A database system beloved of the editor, which allowed for flagging of sets of references for each section of text, and ready addition of mostly-newer (1990's to present) from the MINLIB and WORLD databases. Mid-2017 status:



# The rest of Volume 2

- Glimpses of edited and illustrated slices of 19th century science. Topics dealt with so far include soil science and the hydrogeochemistry of land and sea.


Above: HMS Challenger at work, surveying the world's oceans, 1872.
Top right: Agricola's 1556 masterwork.
Right: a *salitrera* (nitrate mine) in Chile.

# "A History of Geochemistry and Cosmochemistry"

- Stage 4. The editing (etc) continued into volume 2, reaching through the Medieval period, and including some forward reconnaissance of the 19th century. This continues. The structure of the work was affirmed:

- **Vol. 1. Prehistory to 476 A.D. (fall of Roman Empire in the West)**
- **Vol. 2. Dark Ages through Renaissance to the end of the 19th century.**
- **Vol. 3. The 20th century**
- (plus a growing slice of the early 21st century, to ensure all is up to date!).

- Stage 5. Actual publication, actual publisher ..... (?). Paper and e-book formats (?). Volume 1 has been revised from time to time into Sept. 2020, but was complete in pdf format in summer 2017.

# Sources of illustrations, 1

- Unless otherwise indicated, photographs are by GCW.
- Other sources cited, in order of appearance:


- 1. Tutankhamen dagger: image from BBC, 2016 (http://www.bbc.com/news/world-middle-east-36432635).
- 2. Map of early mining, Turkey and Iran: Alex Imreh in Old Europe (undated), at (https://vieilleeurope.wordpress.com/2016/04/03/ethnogenesis-of-europe/)
- 3. Alchemical symbols: Royal Society of Chemistry (http://www.rsc.org/periodic-table/alchemy)
- 4.Touchstones: *https://www.jewelry-auctioned.com/nl/learn/jewelry-how-tos/how-to-understand-the-meaning-of-gold-hallmarks,*
- 5. Sulphur: Wilson, W.E., 2015. The Conil sulfur mine, Cadiz province, Andalusia, Spain; Mineral.Record, v. 46, p. 681-697. Photo © Trustees of the Natural History Museum, London.
- 6. Graphite: Moore, T.P., 2009. Denver Show 2008; Mineral.Record, v. 40, p. 71-82. Photo © Wendell Wilson.
- 7. Diamond: Moore, T.P., 2004. A collection of diamond crystals with notes on the science, history, and worldwide localities of diamonds; Mineral.Record, v. 35 no.1, p. 9-30,53-54,63. Photo © Wendell Wilson.
- 8. Zapotec jade: Ramirez Vasquez, P., 1968. The National Museum of Anthropology, Mexico. Art, Architecture, Archaeology, Ethnography; Harry N. Abrams, Inc., New York, 257pp.
- 9. Islamic glass weights: Newby, M.S., 2000. Glass of Four Millennia; Ashmolean Museum, Oxford University, 80pp.
- 10. Egyptian glass dish: as above, Newby, M.S., 2000.

# Sources of illustrations, 2

- 11. Woodcut based on Ovid: see the compilation of Daniel Kinney and Elizabeth Styron at http://ovid.lib.virginia.edu/notes.html.
- 12. Death of Pliny the Elder: the 1813 painting "The Eruption of Vesuvius" by Pierre-Henri de Valenciennes (1750-1819). See text and illustration from Tom Gidwitz, http://www.vesuvius.tomgidwitz.com/html/the_death_of_pliny.html.
- 13. Map of the Shang dynasty: Cunliffe,B., 2015. By Steppe, Desert, and Ocean: the Birth of Eurasia. Oxford University Press, 530pp.
- 14. Delhi iron pillar, book cover of: Hegde, K.T.M., 1991. An Introduction to Ancient Indian Metallurgy; Geol.Soc.India, Econ.Geol.Ser. 4, Bangalore, 86 pp.
- 15. Abbasids in Baghdad: from 1001inventions.com (*problem with link, 07 Sept. 2020*).
- 16: Visigoth crown: Museo Arqueológico Nacional, 2014. Guide: Museo Arqueológico Nacional, Serrano 13, Madrid 28001, Spain, Engl. transl., 138pp.
- 17. H.M.S. Challenger: reproduction from web pages of NOAA Ocean Explorer (*problem with link, 07 Sept. 2020*).
- 18. Cover of de Re Metallica: Hoover, H.C. and Hoover, L.H, 1912. Translation of Agricola, G., 1556. De Re Metallica; Froben, Basel Folio. Mining Magazine, London, 638 pp. Reprinted 1950 by Dover Publications, Inc., New York.
- 19. Chilean nitrate mine: http://www.memoriachilena.gob.cl/602/w3-article-82507.html, Bibliotheca Nacional de Chile,

- Note: a few illustrations in this presentation are NOT in the current edit of Boyle vols. 1-2.

# "R.W. Boyle's History of Geochemistry, Part I: from Antiquity to Medieval Times“

## Abstract


- Robert Boyle (1920-2003) was a famed geochemist and field geologist. Over a long career at the Geological Survey of Canada, he wrote many influential works, including books on gold, silver, uranium and thorium. He devoted the last two decades of his life to a massive “History of Geochemistry” which, at the time of his death, was a sprawling, unadorned but essentially complete manuscript. The presenter – perhaps rashly – undertook to edit, update, restructure and illustrate what will in due course be a trilogy-size, worldwide examination of human endeavour in the Earth Sciences, mining, metallurgy and technology. Tonight’s show will skim the surface, in a colourful and hopefully entertaining selection of highlights of more than ten millennia of human progress, bringing us to *circa* 1500 A.D.