Ammonia and the *Secretum Secretorum*

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Commemorating the dual 250th Anniversary 1756-2006

Joseph Black: demonstrated gaseous ammonia, Edinburgh

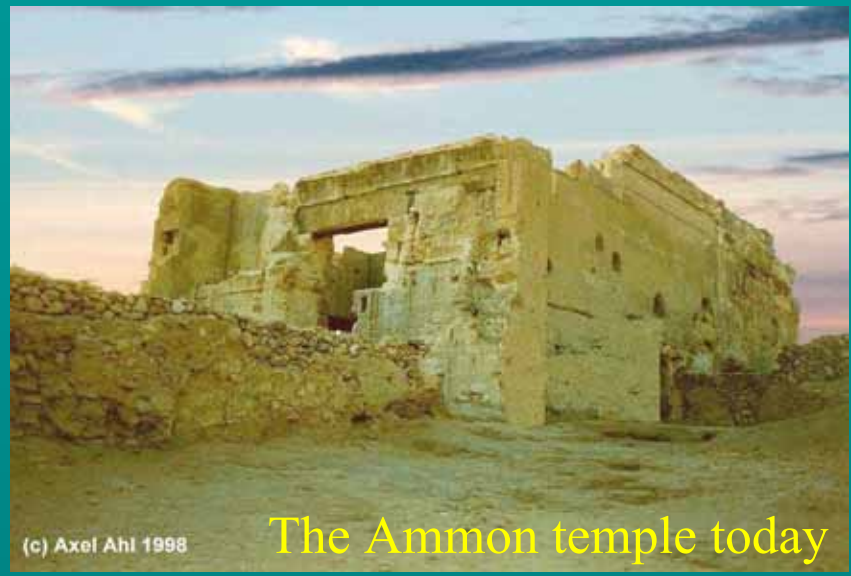
James Davie & James Hutton: established the first European *sal ammoniac* factory, Edinburgh

A fast history of ammonia….

- >1000 years in 30 minutes
- From the present then working backwards
- Origin of scientific knowledge on NH_x?
- Reflect on the messages from history for current NH_x research

The origin of the name "Ammonia"

- "Ammonium" a town at the Siwa Oasis, Lybia:
- "Temple of Ammon": one of the three great oracles of the ancient world
- Αμμοσ = Greek for sand
- Ammon = Ram god, Amun of the sands.
- Major temple with over 80 priests; Oracle consulted by Alexander the Great (331 BC)

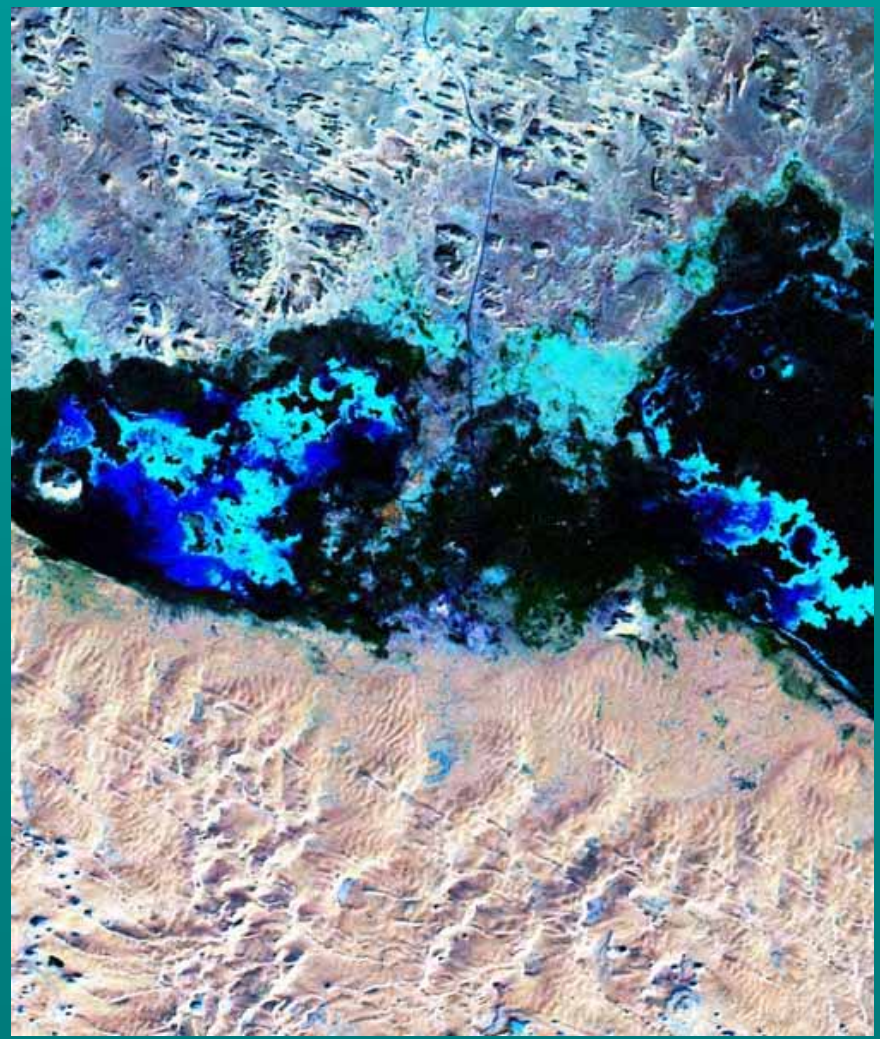


The Ammon temple today


Ammon; Alexander as son of Ammon

Origin of *Sal Ammoniac*: Option A

A. Deliquiescent salt found in the sands, used in Ammon sacrifices and prized in medicine (Pliny, Arrian, Columella etc)

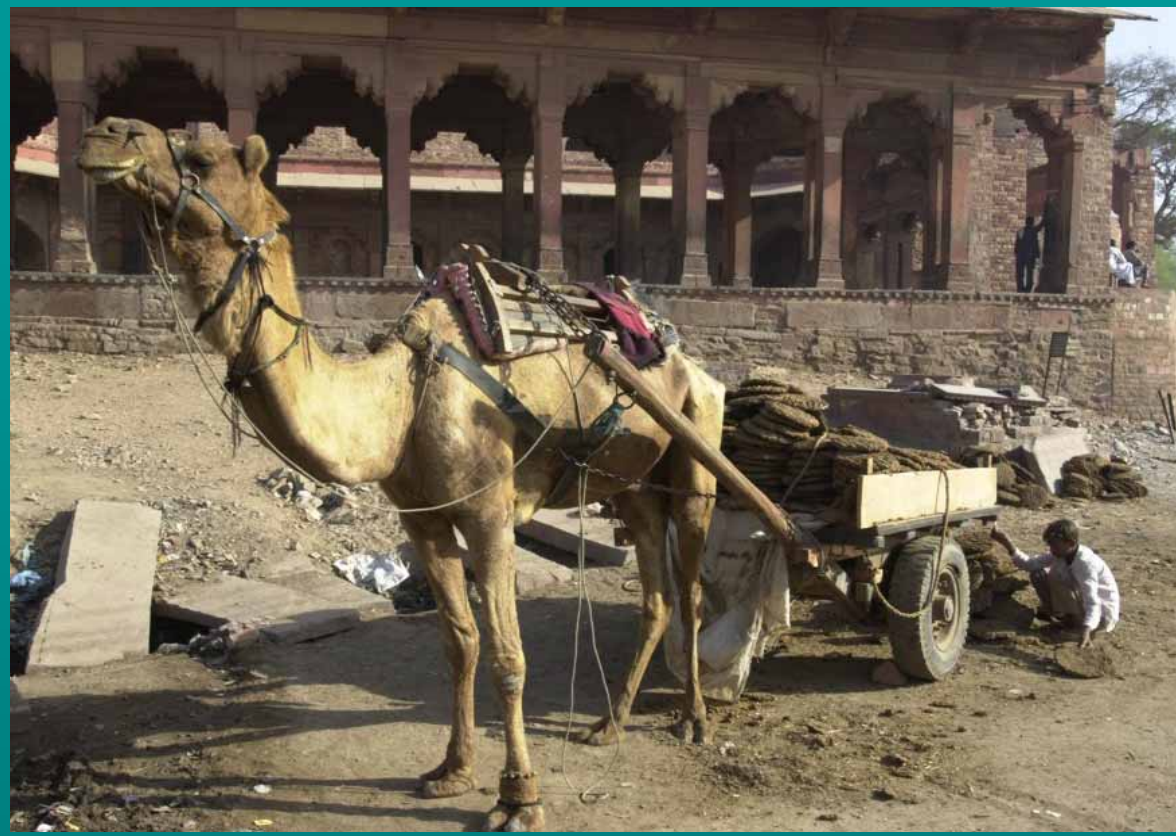


Sal ammoniac = NH_4Cl

Origin of *Sal Ammoniac*: Option B

B. Extract from the plant "Ammoniac": *Dorema ammoniacum*
Used in the temple ceremonies
Pliny: "*The price .. of the best quality is forty asses per pound*"

Origin of *Sal Ammoniac*: Option C



C. The priests found in soot on the temple walls in the soot from their burned sacrifices

Sal ammoniac at ancient Ammonium. The Options

A. Pliny's salt from the sands by the Ammonium Oasis

B. Extract from the plant *Dorema ammoniacum*

C. On the sooty walls of the Temple of Ammon

Your choice!

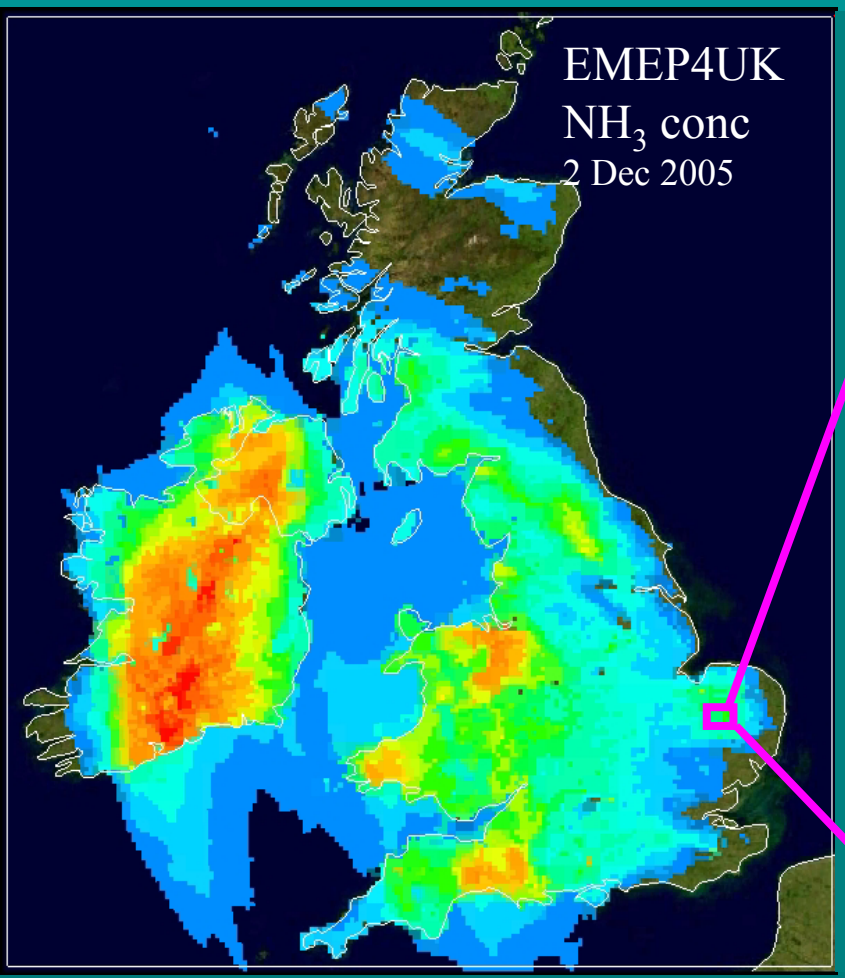
Recent Achievements: The future history

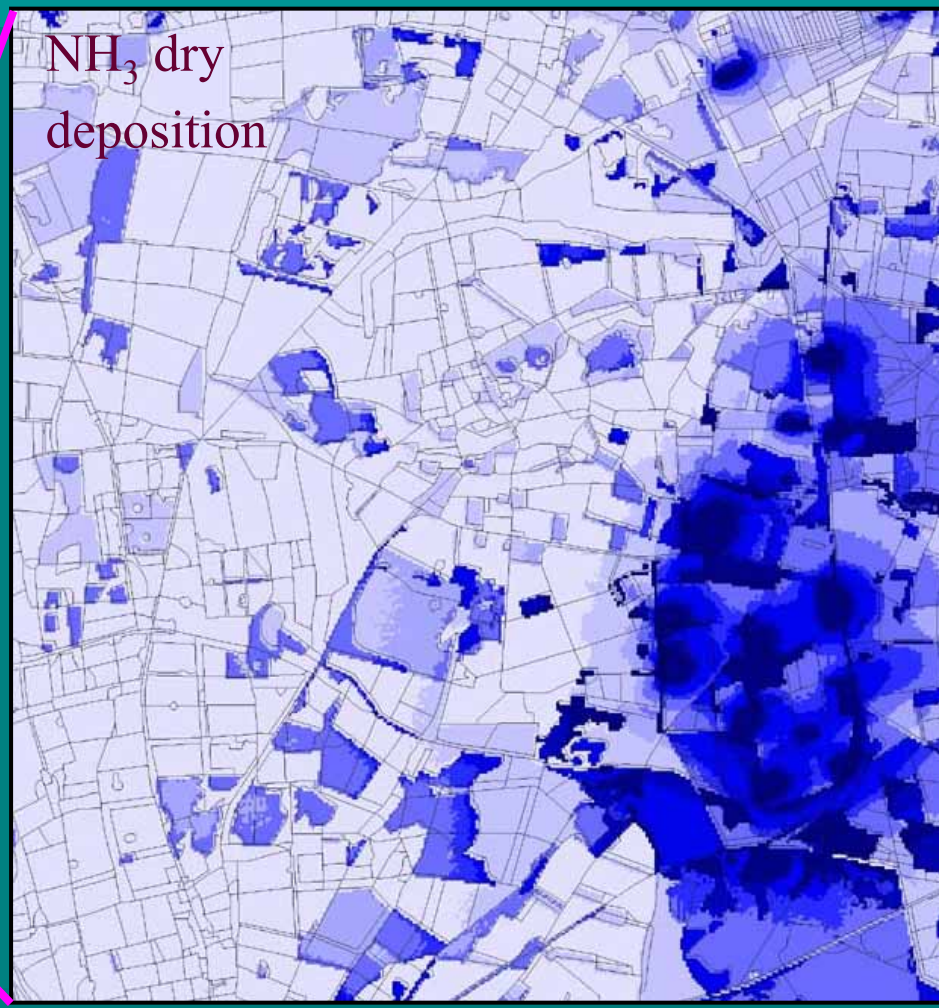
- What were the key NH_x advances of the last 25-30 years?

- Examples:
  - Atmospheric ammonia contributing to acidification and biodiversity loss.
  - Continuous flux measurements and understanding of bi-directional NH_3 exchange
  - Massive data collection leading to comprehensive spatial NH_3 emissions inventories
  - Numerical atmospheric transport models able to simulate atmospheric NH_x and chemistry

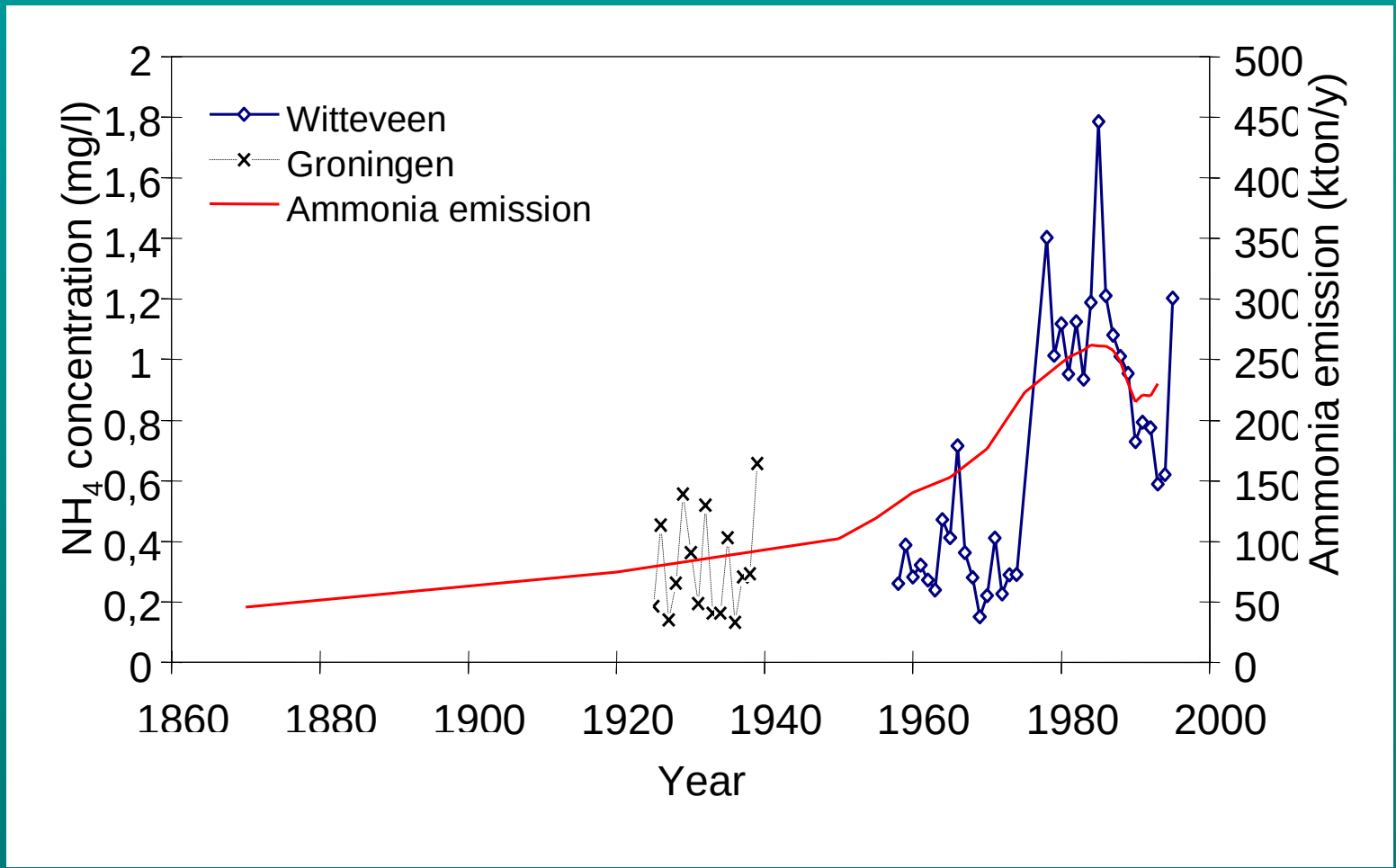
- **Questionnaire: complete by Tuesday AM**

Multi-scale modelling of NH_x





Ammonia emission and precipitation ammonium in the Netherlands



Change in Agriculture after 1950

Nutrient shortage
& priority to conserve

Fertilizer

Increased stock

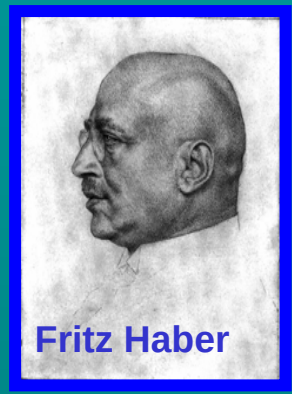
Intensive livestock breeding

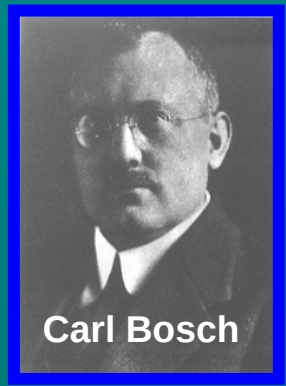
More NH_3 emission

Haber-Bosch Process

- Limited supply of natural nitrate sources
- Haber-Bosch: 200 atmos; 450-500 ºC

  $N_2\,(g) + 3\,H_2\,(g) \Leftrightarrow 2\,NH_3\,(g)$
- Patented 1908 by Fritz Haber
- Commercialized 1910 by Carl Bosch
- Used Ostwald process (1902) to make HNO_3 for NH_4NO_3 production
- For explosives and fertilizers


Fritz Haber


Carl Bosch

Early 20th Century

- Role of atmospheric NH_x as a plant nutrient for agriculture
- Understood well the possibility for ammonia emissions and deposition

- First profile measurements of "dry deposition", Rothamsted (Hall & Miller 1911)
- kg NH_x ha^{-1} yr^{-1} to covered plate collectors:

Height of collector	Broadbalk (Fertilized)	Lawn (unfertilized)
1.15 m	1.28	1.77
0.05 m	1.98	1.02

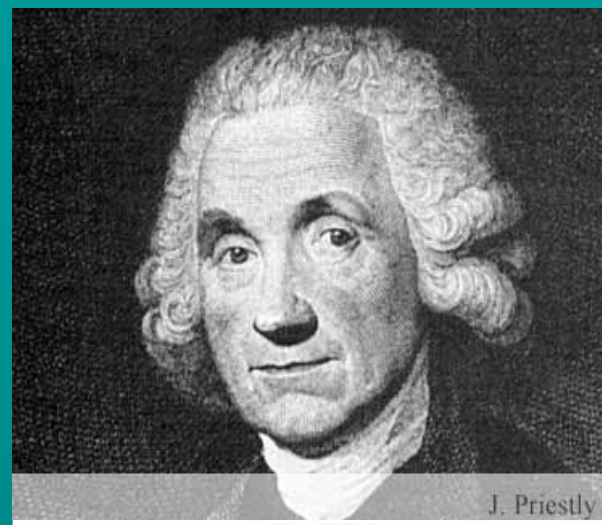
19th Century debate on the source of nitrogen for plants

- De Saussure (1804): Early studies of plant N nutrition. Demonstrated the presence of NH_3 air
- Liebig: Argued that plant N would be obtained from atmospheric NH_x, like CO_2.
- Lawes & Gilbert, and Way at Rothamsted showed that inputs of wet deposition were insufficient for crop growth. Demonstrating the importance of soil N.
- Ville, Schlosing etc. 1850-1900: First atmos. NH_3 conc. measurements across Europe. Highest values in cities

De Saussure (1804)

18th Century Discovery of Ammonia in Air

- Joseph Black (1756) : Thesis University of Edinburgh. Demonstration of the volatile alkali on adding lime to *sal ammoniac*
- Joseph Priestly (1774): Captured the gas liberated above heated spirit of hartshorn in a trough above mercury "alkaline air", reacted it with HCl and made *sal ammoniac*
- Karl Wilhelm Scheele (1777) Showed alkaline air contains nitrogen
- Morveau / Bergmann (1782) Named it "ammonia"
- Claude-Louis Berthellot (1785): Showed that the chemical composition was 0.81 g N : 0.19 g H.



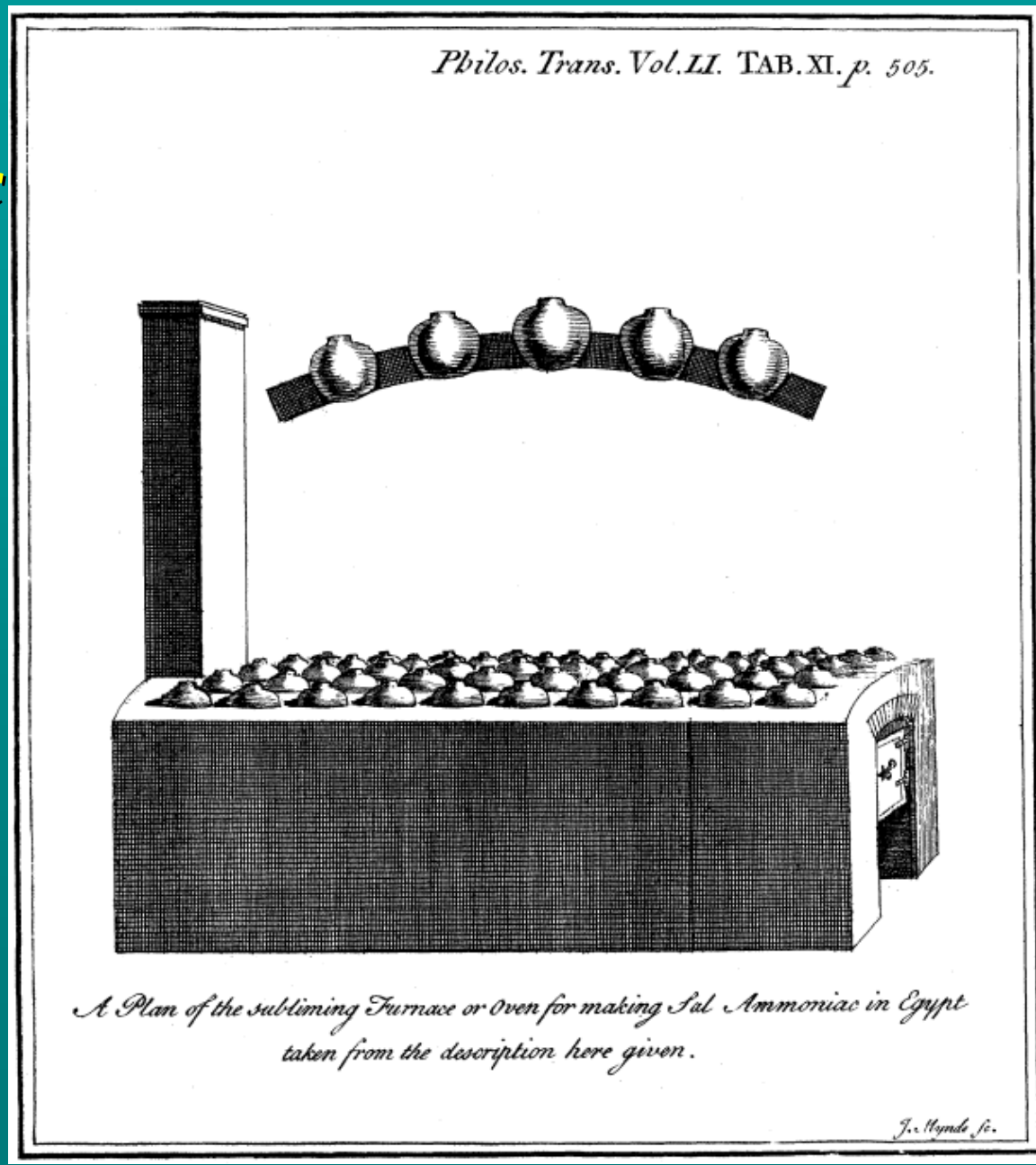

Berthollet

18th Century Debate on the source of *sal ammoniac*

- Long running debate at the Academie Francais
- Imported from Egypt since 12thC, but the process unknown and kept secret by Venetian traders.
- Pliny's description of *sal hammoniacum* doubted.
- Geber (13th C) & Glauber (1567) claimed by boiling down urine, NaCl & soot (5:1:½). Later shown this was not effective: was it deliberate mis-information?
- Siccard (Academie Francais) and later Lineaus reported to Royal Society (1760) the detailed process.

Lineaus, Hasselquist & Ellis on: Egyptian *Sal ammoniac* manufacture (1760)

- Soot from Spring dung (from legume grazing) was collected from peasants & placed in jars
- Jars gradually heated above a furnace until it reached "hell fire" (>300 °C)
- Sublimed *sal ammoniac* collected in necks of glass vessels



The first European *sal ammoniac* factory

James Davie & James Hutton (1756), Edinburgh

- Secrecy over the process
- Appears they broadly followed the Egyptian approach

- They used the soot of coal fires
- Took ALL the soot of the *Tronmen* society of Edinburgh sweeps
- 26 kg of soot yielded 6 kg of *sal ammoniac*

19thC Edinburgh from the NW

From Session Papers in the Library of Writers to the Signet

Ammonia in European alchemy

- Arrival in Europe: *Sal ammoniac* known from ~1140 AD Latin translations of Arabic alchemy texts
- Four spirits of medieval alchemy: mercury, sulphur, arsenic and *sal ammoniac*
- Spirit of Hartshorn: NH_4CO_3 from distillation of horn, bone, offal etc
- The key to *Aqua Regia*: $NH_4Cl + HNO_3$ dissolves gold. First step to making gold…
- Fulminating Gold: $AuNH.NH_2$. (attrib. Valentinus 15th C) Precipitate out AuOH, then add Spirit of Hartshorn. The most expensive explosive. Used in Battle: Dutchman for English vs French in 1628!

- The Emerald Tablet and the search for the elixir, the philosophers stone….

Isaac Newton and the Emerald Tablet

- Newton also an alchemist and translated the *Emerald Tablet* - mystic text of 12 lines.

  7a. Seperate thou ye earth from ye fire, ye subtile from the gross sweetly wth great indoustry.

  8. It ascends from ye earth to ye heaven & again it desends to ye earth and receives ye force of things superior & inferior.

- It was believed to contain the full secret of Medieval alchemy – to the initiated…
- Appeared the *Secretum Secretorum* of Roger Bacon (1255). and attrib. to *Hermes* (Egyptian 400 BC?)

Newton's experiments with alchemy ~1680

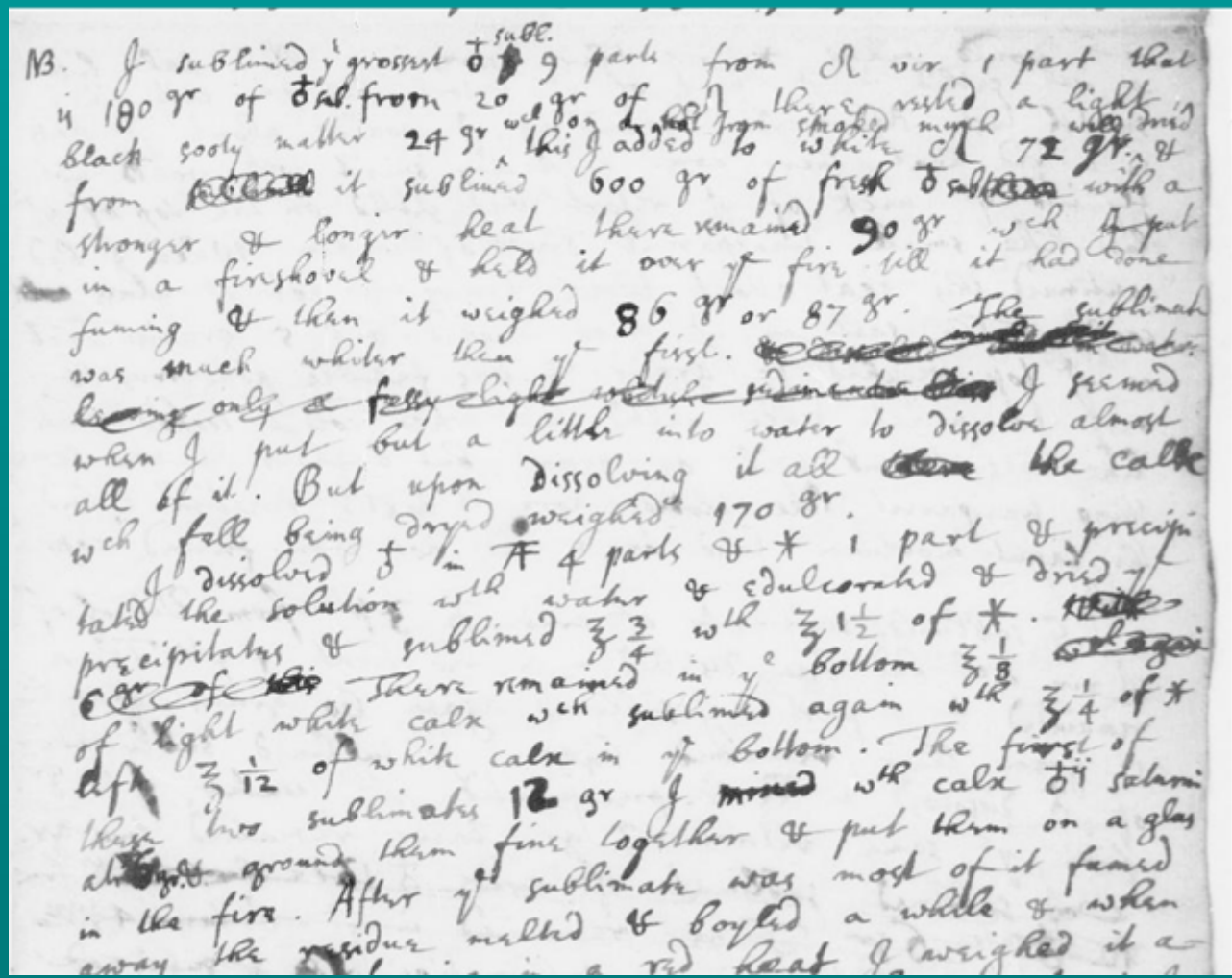
I sublimed ☼ & ♃ana. Of this sublimate I took an ounce & 1/2 an ounce of ♄♃tiate & sublimed them.

.. there arose a little salt like ☼ which … had a sweetish tast.

☼ Sal ammoniac

♃ana Antimony ore

♄♃tiate Lead antimonate



Arab origin of Alchemy and ammonia

Convention:

Discovered NH_x in 9th C Iraq

- **Ibn Jābir:** *sal ammoniac*, *Aqua Regia*
- **Al Razi:** Spirit of hartshorn

Current understanding

- Jābirian Corpus – by many authors
- Exploited NH_x but not discovered.
- Earliest copy of *Kitāb Sirr al-Asrār*
- From earlier texts: Trans-Oxiana, China?

Uses of *sal ammoniac*

- Colour and dissolve metals
- Reduce metal oxides, for tinning etc.
- Dying cloth, glass pigments
- Medical: chest, Hg antidote etc

Sources of NH_x in Arab times (texts from c. 930-970 AD)

Sal ammoniac (NH_4Cl)

- Al-Mas'ūdī, Al-Muqaddasi: Naturally burning coal seams in Transoxiana and China
- Ibn Hauqual: Damindan volcano, SE Persia (Others called it "a smoking fountain of hell")
- Al-Maquaddasi: Sicily – but the supply already exhausted
- Al- Istakhrī: From Egypt, by sublimed soot of burned camel dung at the Baths

Spirit of Hartshorn (NH_4CO_3)

- Al-Razi and others: Distillation of Hair and offal for NH_4CO_3: New in Arabia?

Abufeda (1321), Von Lippmann (1919), Needham (1980)

Changing names of NH_4Cl

Major variants only!

- Ammonium chloride (English, 19th-21st C)
- Sal ammoniac (Latin, 12th -19th C) (Egyptian source)
- Sal armoniac (Latin, 10th-15th. C) (Armenian source)
- Almisader, Mizadir (Latin, 12th-15thC)
- Nushadir (Arabic, 9th-present)
- Nao Sha (China, 1st C- present)
- Nao (China, origin unclear)

Possible etymology

Nao = impure Nao Sha (J. Needham FRS FBA, 1980 favoured)

Sha = sand/granules

Dur = medicine? (Stapleton, 1905)

Chinese origin *sal ammoniac*?

Wei-Po Wang: *Tshan Thung Chhi* (142 AD)

"It would be like mending a cauldron with glue, or bathing a boil with sal ammoniac, or driving away cold with ice…."

BUT

Su Jing: *Tang Ben Cao* (658-659 AD)

"Nao Sha orginated from tribesmen at the western border of the Zhou dynasty" (1000-200 BC)

- Tarim Basin (Xing Jiang) the source of burning coal fields
- Tarim was Iranian speaking, e.g. Sogdians
- Movement of culture was from the west: Zoroastrianism, Buddhism, Manicheism, Nestorian Christianity (500 BC – 500 AD)
- Iranian Magi (Zoroastians) as priests at the Chinese Zhou court (1000-200 BC)

Western peoples in ancient Tarim

Mummy from Zaghunluq
Tarim Basin, (~1000 BC)

Zoroastrian & Mithraic origins of sal ammoniac

- Bactria, Fergana, Sogdia: popn. 1 million
- The *other* fertile crescent (from 3000 BC)
- Eternal coal fires at several locations
- Mithraic & later Zoroastrian Fire 'worship'
- NushAdar: hero, 4th generation after Zoroaster (~400-500 BC?)

Etymology:

- Nush = Immortal; Adar = Fire

later variant:

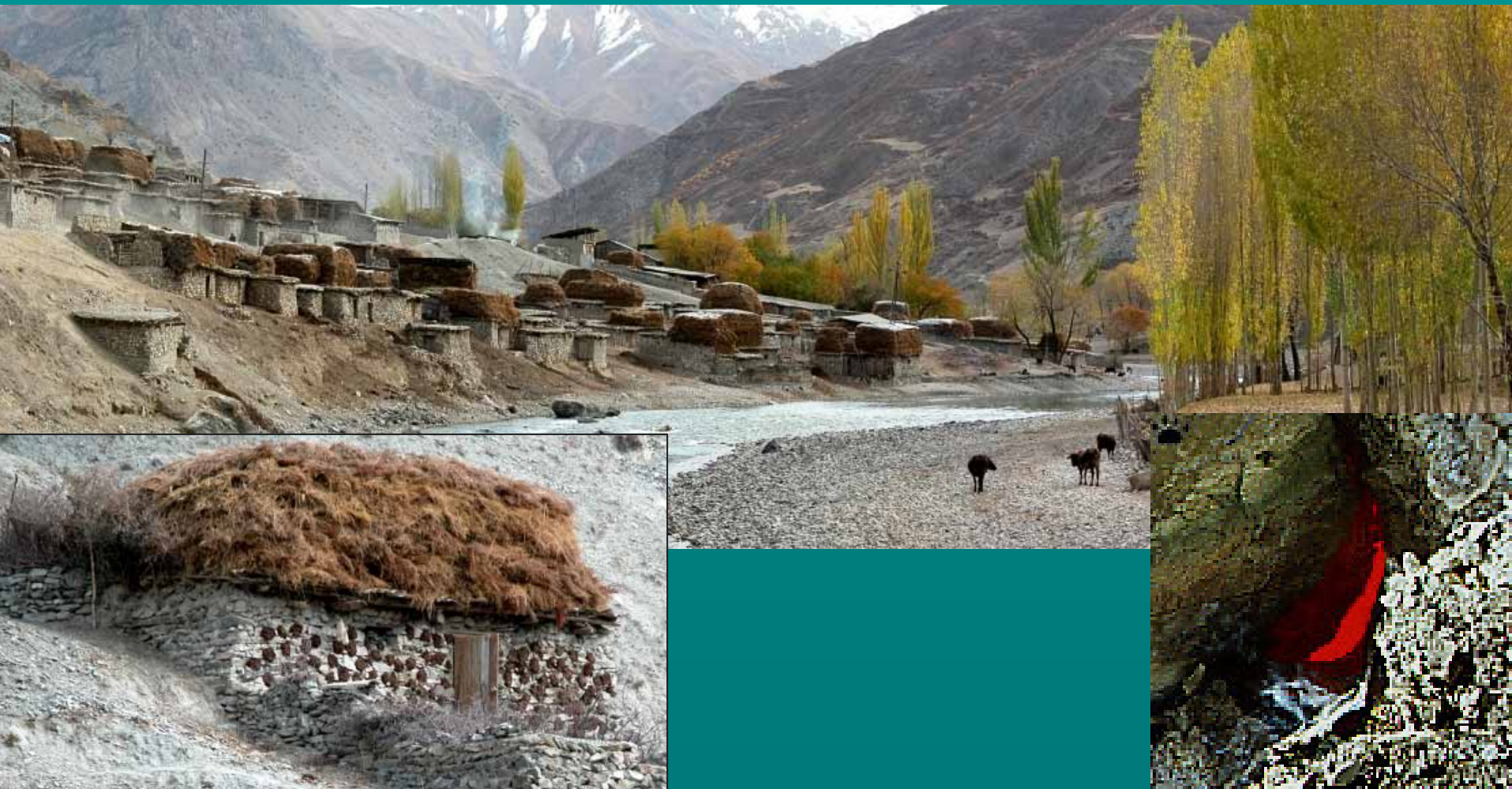
- Nush = Elixir or Antidote

Ahura Mazda & sacred fire

Fire temple, Perseopolis

Anzob, upper Zerefshan (Tajikistan)

- Burning coal caves visited by Alexander
- Rich deposits of Au, Hg, Ag, Sb etc.



Assyrian Evidence of *Sal ammoniac* (~500 BC)

Ahura Mazda & Sphinxes

In pigments?

- To make Lead Antimonate $Pb_3(SbO_4)_2$ (Naples Yellow) used in glazed tiles

In Sumerian Cuniform texts?

- IM.KAL.LA = sublimate of soot = *sal ammoniac* (Thompson, 1933)

Zozimus (Egypt, 300 AD) on the Elixir

- Alchemist, gives his interpretation of Agathodaimon (? BC),
- Noting the properties of the philosopher's stone he writes:

This is the uncommunicated mystery which none of the prophets dared to divulge in words but revealed only to the initiated.

In their symbolical scriptures they called it the stone which was not a stone, the thing unknown and yet known to everyone, the despised thing of great price, the thing given by God and yet not given.

For my part I shall praise it… for it is the one thing which dominates matter.
Such is the drug of power, the Mithraic mystery.

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Conclusions
Sal Ammoniac at the Temple of Ammon?

A. Pliny's salt in the sand? It was a prized NaCl. Europe looked for parallels in classical writers. Or a traders trick.

B. The plant extract? *Gum Ammoniac* came from the town of Ammonium, but no NH_x in it. The red herring.

C. Crystals in the Temple Soot? 18thC Historical extrapolation…

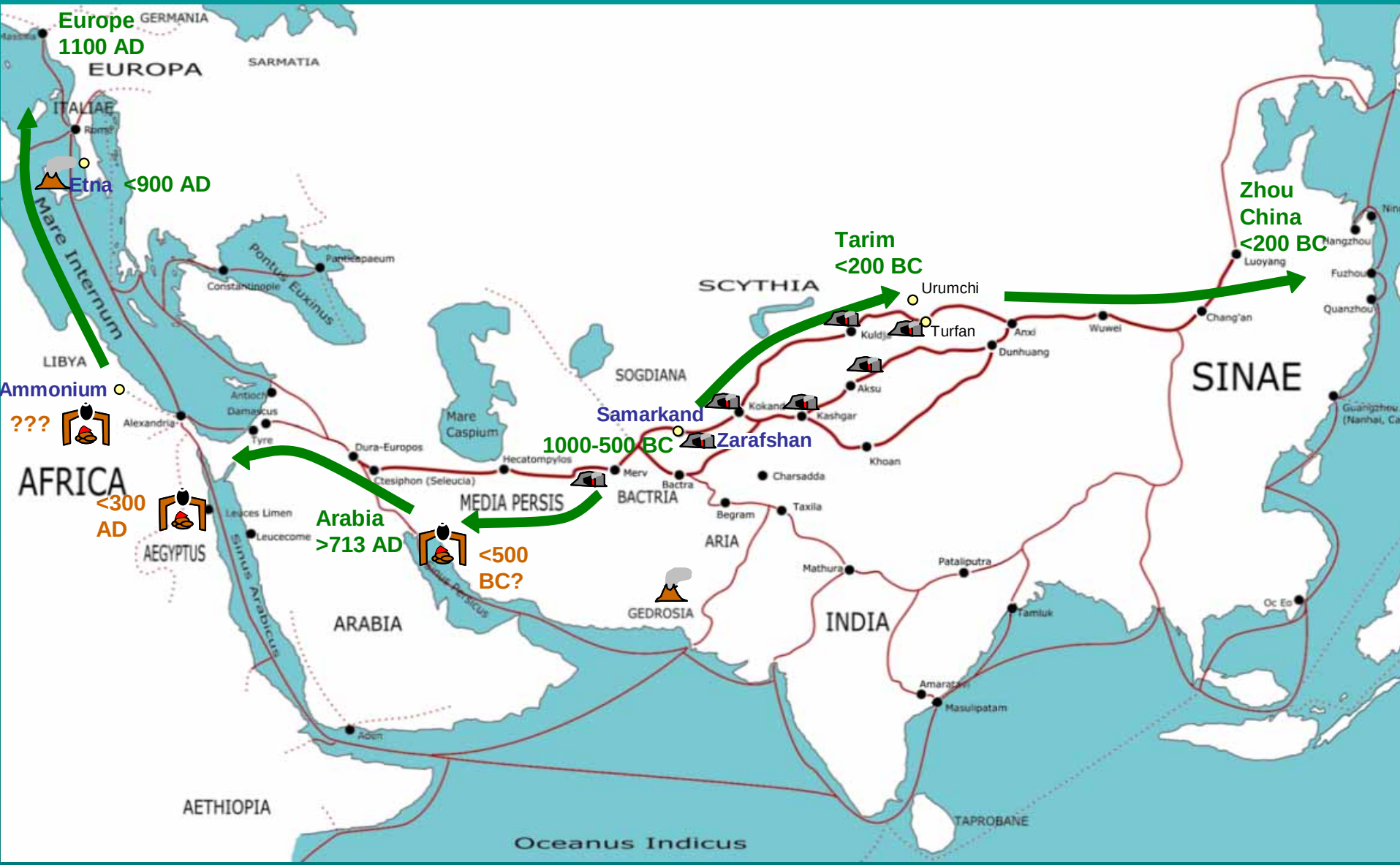
But NH_4Cl from soot sublimation in Egypt was:

A major industry in ~950 AD

Probably known by Zosimus (300 AD)

Possibly known by Agathodiamon (? BC)

Spread & *sal ammoniac* along the Silk Road



Conclusions and our NH_x research

Tend to forget the understanding of previous cultures
The recollection sets perspective.

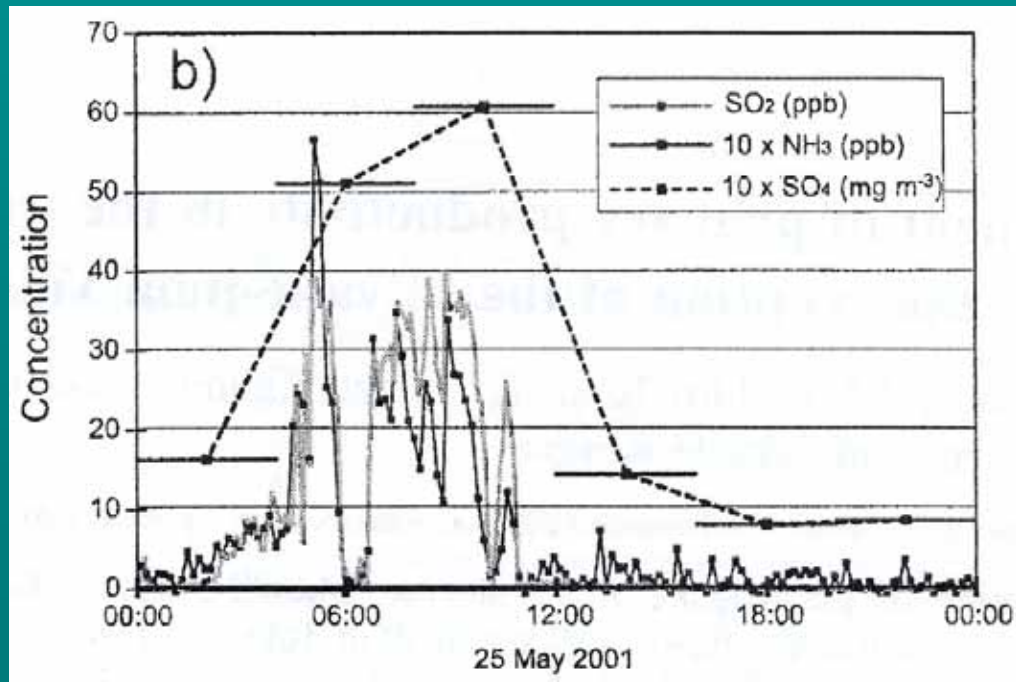
The original sources of NH_3 are hardly studied:

- NH_3 from Dung burning (no literature)
- Direct NH_4Cl from all biomass burning (missing)
- NH_3 & NH_4Cl from coal combustion (minimal data)
- NH_3 and NH_4Cl from volcanoes…..

Volcanic ammonia & *sal ammoniac*

- Le volcan de la Soufrière, Guadeloupe "Many fumeroles give off an unpleasant odour of rotten eggs & ammonia"
- Uematsu et al. (2004) *Geophys Res Lett.*

Mijake-jima emission: 300 kt NH_3 per year!



100 km from Mijake-jima, Japan