



Making minerals from seawater

by

Professor R A Mills

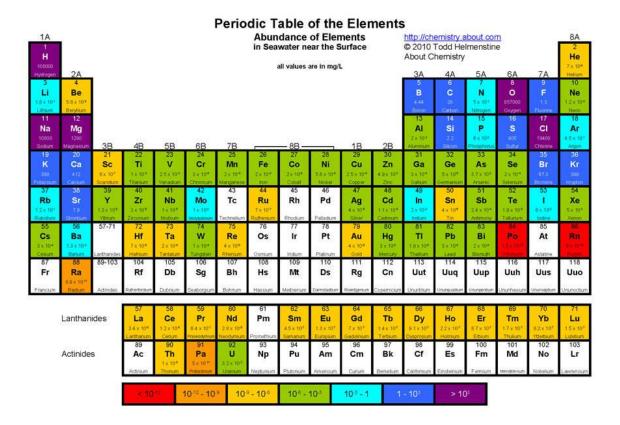
The LRET Research Collegium Southampton, 16 July – 7 September 2012



Making minerals from seawater.

Professor Rachel A Mills National Oceanography Centre, Southampton 19 July 2012

Seawater Composition



http://chemistry.about.com

Trace metals in the oceans

- Trace metals are present in seawater at extremely low levels
- These metals are vital for cellular biological processes
- Our understanding of the sources, fluxes and timescales for removal of metals from seawater is still poor
- Metals are removed from seawater to form mineral deposits at the seafloor
- As the demand for metals increases, the feasibility of ocean mineral resources increases



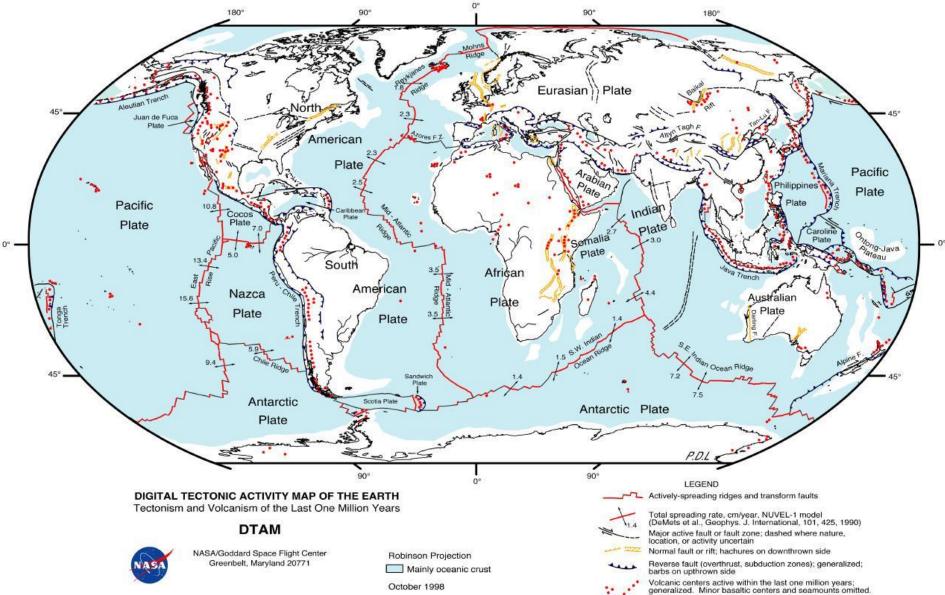
How are minerals formed in the ocean?

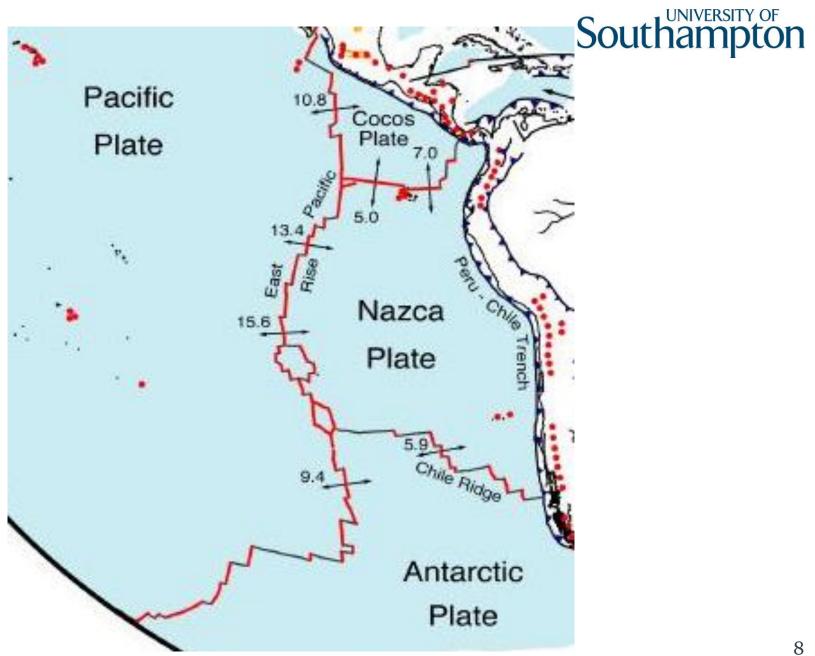


- 1. Hydrothermal deposits and seafloor minerals
- 2. Hydrothermal plumes and metalliferous sediments
- 3. Manganese nodules and crusts

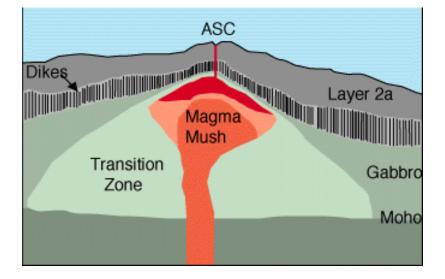




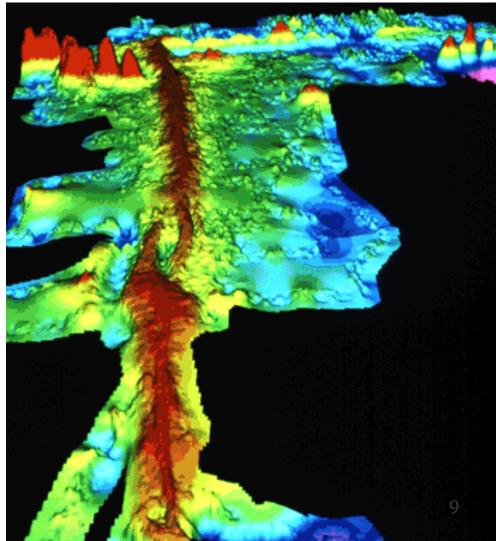




Southampton Schematic cross section through the East Pacific Rise

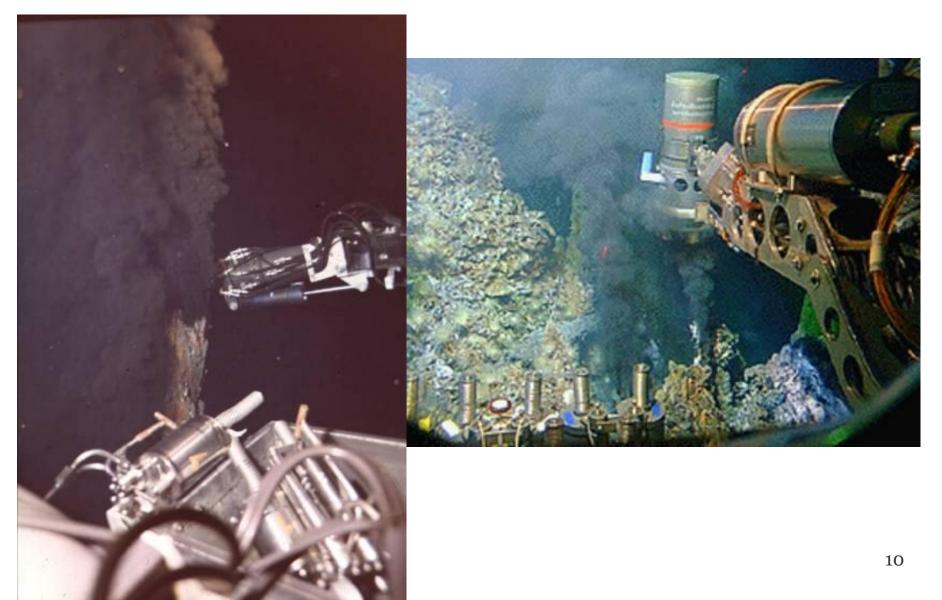


ASC = Axial Summit Caldera

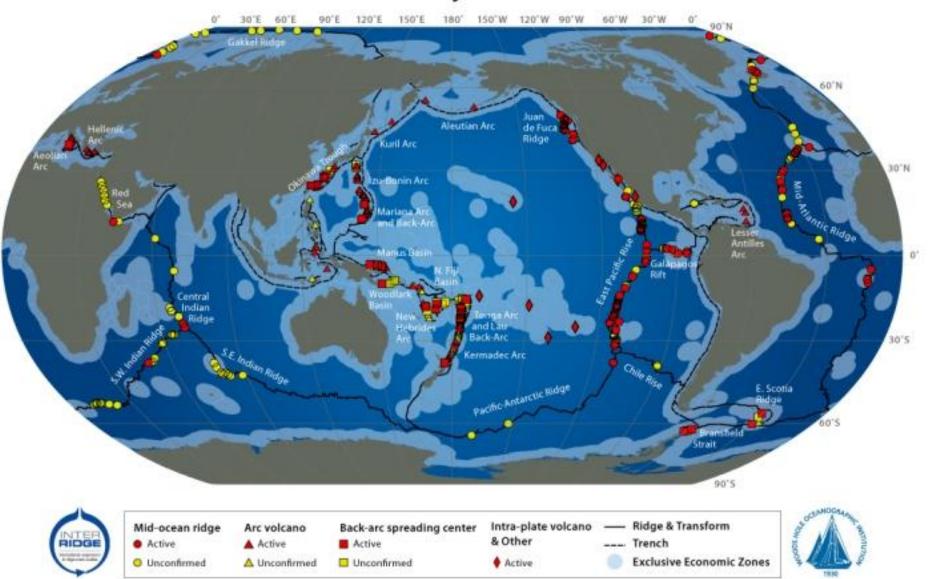


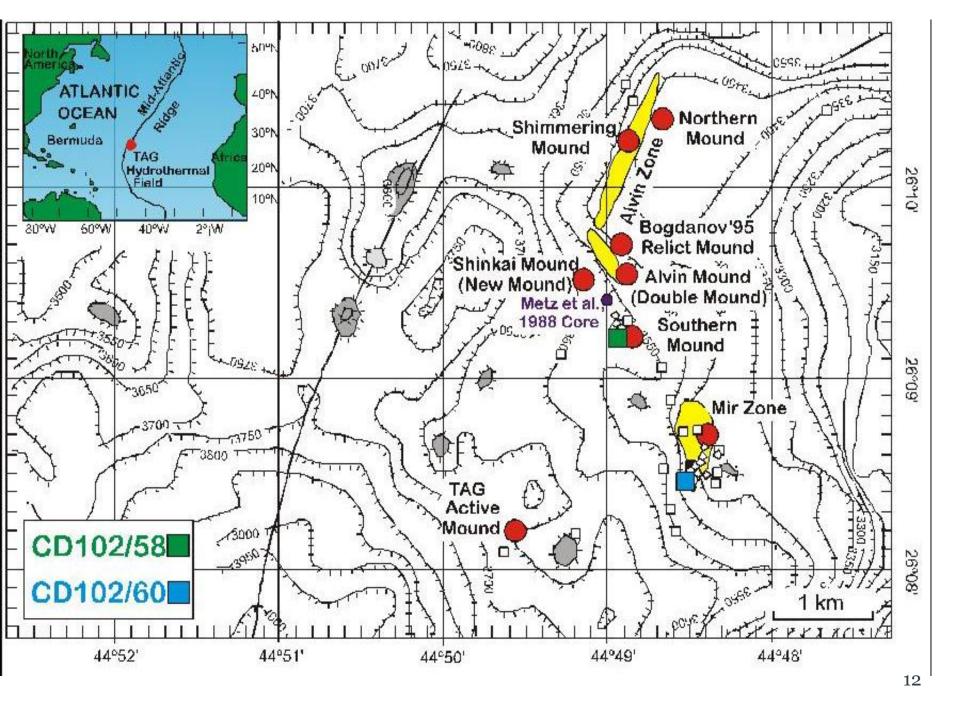
High temperature fluid expulsion at seafloor

Southampton

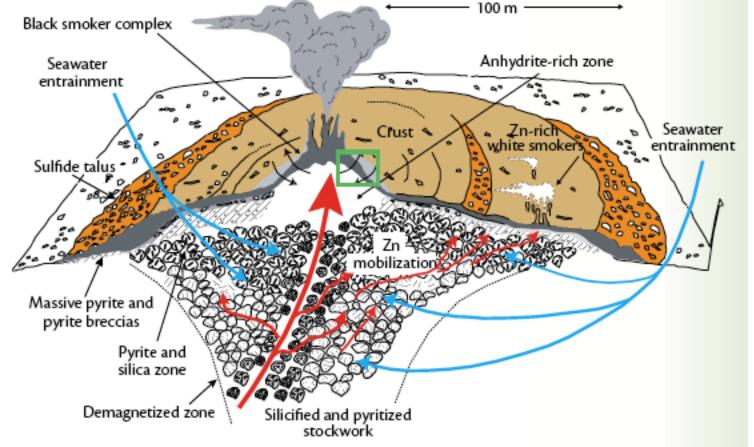


Global Distribution of Hydrothermal Vent Fields





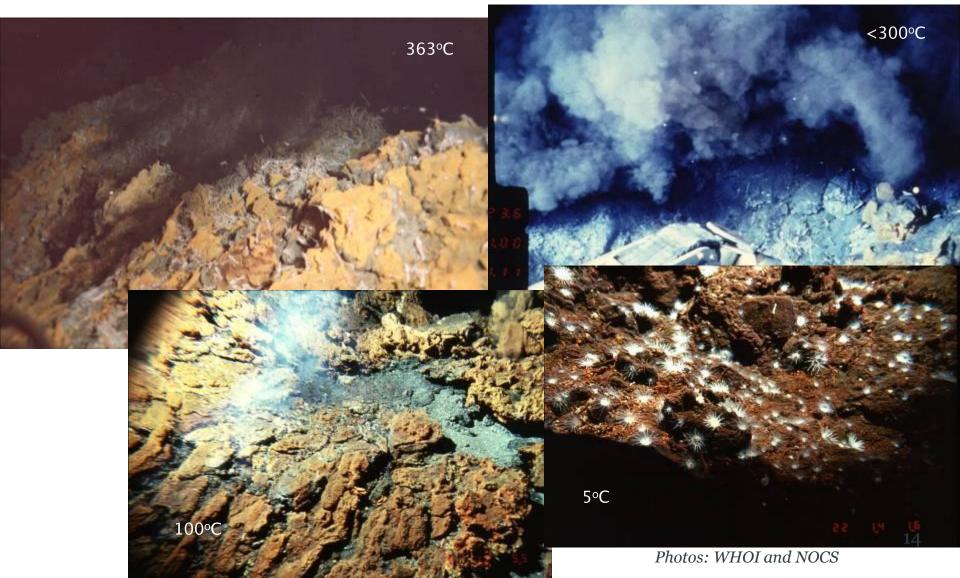
Southampton Anatomy of an active hydrothermal mound



Tivey, 2008, adapted from Humphris et al., 1995

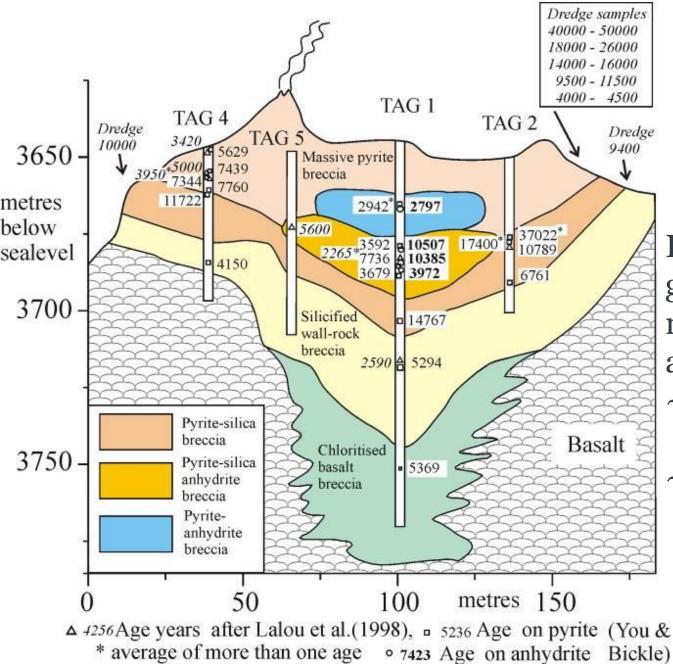
Fluid flow out of an active hydrothermal deposit

Southampton



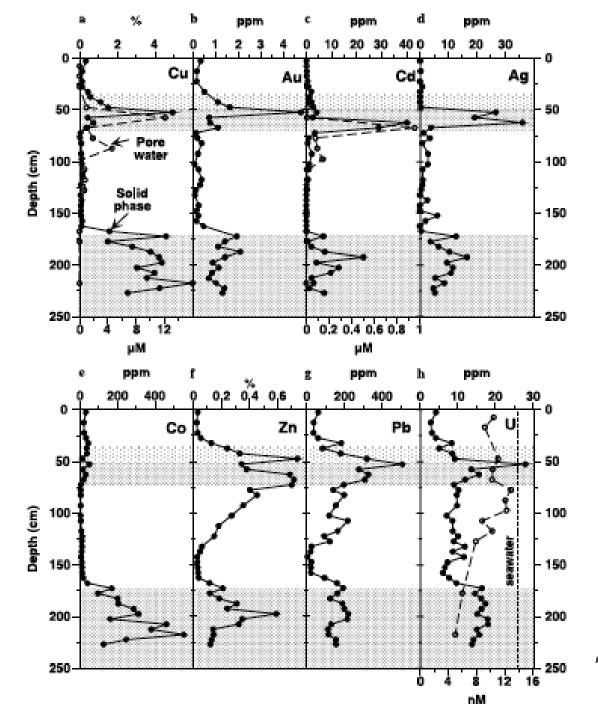


How fast do deposits form?



Episodic mound growth, oxidation, reworking of sulfide and anhydrite over ~10 000 years

~ 5 Mtonnes sulfide



High grade metal enrichment (several parts per million to %) indicates significant redox recycling and secondary mineralisation over thousands of years

Severmann et al., 2006

Southampton Seawater and the Rare Earth Elements (Lanthanides)

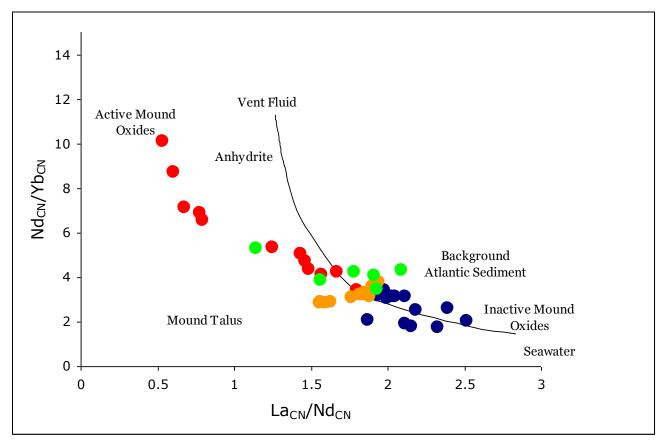
| | | | | | | Perio | dic T | able | of the | e Eler | nents | 5 | | | | | |
|-----------------------|----------------------|--------------------------------|---|-----------------------|--|----------------------------------|-----------------------------------|----------------------------------|----------------------------------|-------------------------------|----------------------------------|----------------------|-----------------------------|-----------------------------------|----------------------------------|------------------------------------|-------------------------------|
| 1A 1 H | | | Abundance of Elements http://chemistry.abou in Seawater near the Surface © 2010 Todd Helmer About Chemistry | | | | | | | | | | Imenstin | | | 8A 2 He | |
| 108000 Hydrogen 2A | | | | | all values are in mg/L | | | | | | | 3A | 4A | 5A | 6A | 7A | 7 x 10 ⁴ Helium |
| Hydrogen 3 | 2A 4 | 4 | | | | | | | | | 5 | -4A 6 | 5A 7 | 8 | 9 | 10 | |
| Li | Be | | | | | | | | | | в | С | N | 0 | F | Ne | |
| 1.8 x 10 ⁺ | 5.6 x 10* | | | | | | | | | | | 4:44 | 28 | 5 x 10 ⁻⁴ | 857000 | 13 | 1.2 x 10 |
| Lithium 11 | Beryllium 12 | | | | | | | | | | | Boron 13 | Carbon 14 | Nitrogen 15 | Oxygen 16 | Fluonne 17 | Neon 18 |
| Na | Mg | | | | | | | | | | | A | Si | P | S | CI | Ar |
| | 1290 | 199102 | | | | | | | | | | 2 x 10* | 22 | 6.x 10+ | 905 | 19400 | 4.5 x 10 |
| Sodium | Magnesium | 3B | 4B | 5B | 6B | 7B | - | - 8B - | - | 1B | 2B | Aluminum | Silicon | Phosphorus | Sultur | Chlorine | Argon |
| 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 399 | 412 | 6x 10 ⁴ | 1 x 10 ⁻² | 2.5 × 10 ² | 3 x 10* | 2 × 10 ⁻⁴ | 2 × 10 ⁻⁹ | 28.104 | 5.6 x 10* | 2.5 x 10* | 4.9 x 10 ⁴ | 3 x 104 | 5x 104 | AS 3.7 x 10 ⁴ | 2 x 10 ⁻⁴ | 67.3 | 399 |
| otassium | Calpum | Scandium | Titanum | Vanadium | Chromium | Manganese | iron | Cobalt | Nickel | Copper | Zinc | Gallum | Germanium | Arsenic | Selenium | Bromine | Krypto |
| 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 |
| Rb | Sr | Y | Zr | Nb | Mo | Тс | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Те | | Xe |
| 2 x 10 ⁻¹ | 7.9 Strontium | 1.3 x 10 ⁴ Yttmm | 3 x 18 ⁴ Zirconaum | 1 x 10 ⁻⁶ | 1 x 10 ² Monobelenum | Technetium | 7 x 10 ⁻⁷ Ruthenium | Rhodium | Palladium | 4 x 10 ⁴ Silver | 1.1 x 10 ⁻⁴ Cedmam | 2 x 10 ⁻² | 4 x 10* | 2.4 x 10 ⁴ Artimony | 1.9 x 10 ⁴ Telunum | 6 x 10 ^a lodrae | 5 x 10 Xenon |
| 55 | 56 | 57-71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 |
| Cs | Ba | | Hf | Та | w | Re | Os | Ir | Pt | Au | Hg | TI | Pb | Bi | Po | At | Rn |
| 3 x 10 ⁴ | .1.3 x 10* | 5700 55 | 7 x 10* | 2 x 10* Tantalum | 1 × 104 | 4 x 10* Rhenum | 0201 | 332 | 1200 | 4 x 10* Gold | 3 x 10* Mercury | 1.9 x 10* Thallum | 3 x 10 ⁴ Lead | 2 × 10* | 1.5 ± 10# | S-22076 | 8 = 101 |
| Cesium 87 | Banum 88 | Lanthanides 89-103 | Hatnium 104 | 105 | Tungsten 106 | 107 | Osmium 108 | Indium 109 | Platnum 110 | 111 | 112 | 113 | 114 | Bismuth 115 | 116 | Astatine 117 | 118 |
| Fr | Ra | 00071010080 | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn | Uut | Uuq | Uup | Uuh | Uus | Uuc |
| rancium | 8.9 x 10** Radium | Actinides | Rutherfordium | Dubnium | Seaborgium | Bohnum | Hassium | Metherium | Damstadtum | Roentgenium | Copernicium | Ununtrium | Ununguadium | Unurperdum | Ununhexium | Ununseptum | Ununocti |
| | | | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| Lanthanides | | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Но | Er | Tm | Yb | Lu | |
| | | | 3.4 x 10 ⁴ | 1.2 × 10* Cerium | 6.4 x 10 ⁻⁷ Praseodymium | 2.8 x 10* Neodumium | Promethium | 4.5 x 10 ⁺ Samarum | 1.3 x 10 ⁺ Fumpium | 7 x 10* Gadolinium | 1.4 x 10 ⁺ Terteim | 9.1 x 10* | 22x10* Holmum | 8.7 × 10 ⁷ Ethum | 1.7 x 10 ⁻⁷ | 8.2 x 10 ² Viterbium | 1.5 x 1 |
| | Actinides | | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
| | | | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
| | | | Actinum | 1 x 10* Thorum | 5 x 10 ^{-H} Protectinium | 3.2 x 10 [±] Uranium | Neptunium | Plutonium | Americium | Curium | Berkelium | Californium | Einsteinium | Fermum | Mendelevium | Nobelium | Lawrence |
| | | | < 10 | 12 | 10 ⁻¹² - 10 | 9 10 | ⁹ - 10 ⁻⁶ | 10 ⁸ - | 10-3 | 10 ⁻³ - 1 | 1 | - 10 ³ | > 1(| D ³ | | | |

http://chemistry.about.com 18

Rare Earth Elements (REE)

- Relatively abundant (~ppm) in crust but dispersed widely
- Global commercial reserves of REE, particularly the heavy REE are diminishing rapidly
- Global requirement (120 000 tonnes yr⁻¹) exceeds current supply
- Very low abundance in seawater (~10⁻⁷ ppm)
- Forming minerals from seawater fractionates and concentrates the REE

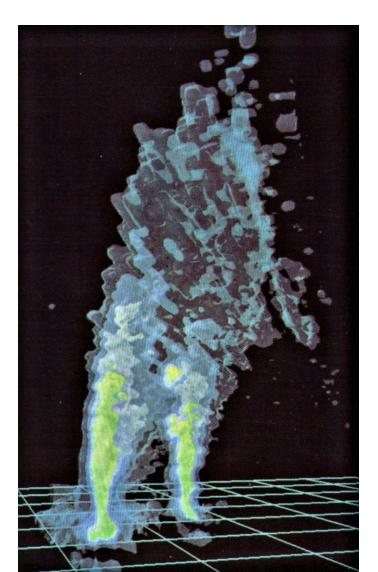
REE fractionation in hydrothermal minerals

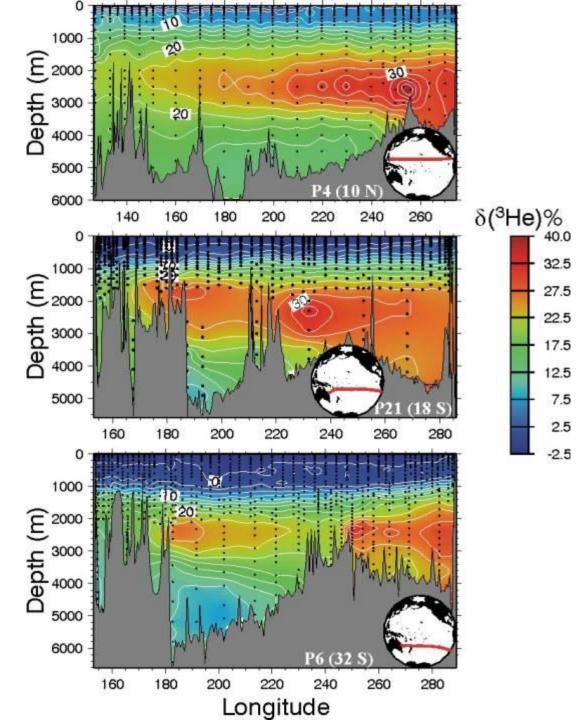


Data from Mitra et al., 1990; German et al., 1993; Mills and Elderfield, 1995; Humphris, 1998; Goulding et al., 1998; Severmann et al., 2004; Mueller et al., 2009

Hydrothermal plumes

- Vent fluid mixes rapidly with seawater and is dispersed through the ocean basin as a plume of particles
- Whole ocean is cycled through global plume system in ~10 000 yrs
- Plumes particles scavenge REE from seawater





Inert tracer shows that hydrothermal plumes are dispersed right across ocean basins

32.5

27.5

22.5

17.5

12.5

7.5

2.5

-2.5

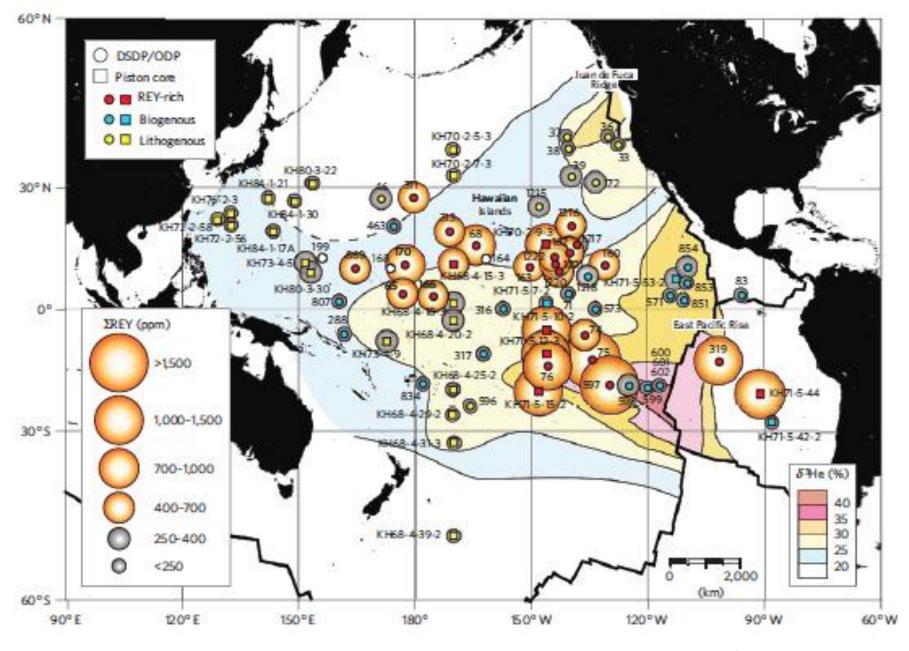
Metalliferous sediments

80° 180°W 160° 140° 120° 100° AL ratios x 100: AI+Fe+Mn 40°N >60 60 - 40 10 - 20- 10 CREST OF ACTIVE RIDGE - 20° 0° 20° 40°S

Plume particles settle to sea floor and form metalliferous sediments over ~Ma (million years)

^s Bostrom and Peterson, 1969

Southampton



Kato et al., 2011

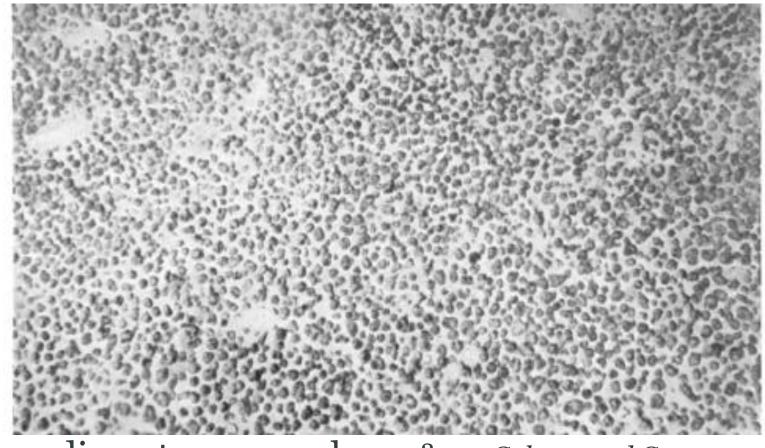
REE resources in metalliferous sediments

- 1 5 km² area of Pacific sediment, 10-70 m thick would supply significant proportion of the global REE demand
- REEs could be recovered through simple acid leaching of the sediment

BUT.....

• Detailed mapping of the resource required and there are significant logistical issues around deep sea mining

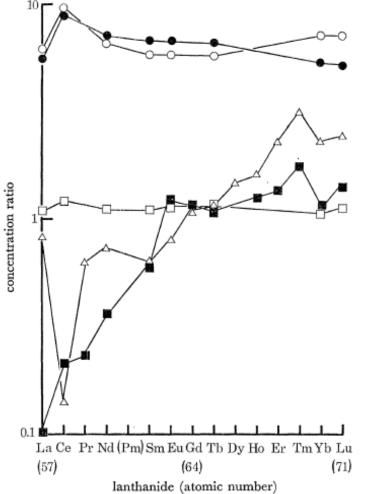
Manganese nodules cover the Pacific seafloor at 4-6 km depth



2-5 cm diameter; 10-40 kg m⁻² Calvert and Cronan, 1978



REE in Mn nodules



 $Mn\,nodules$

Seawater x 10⁷

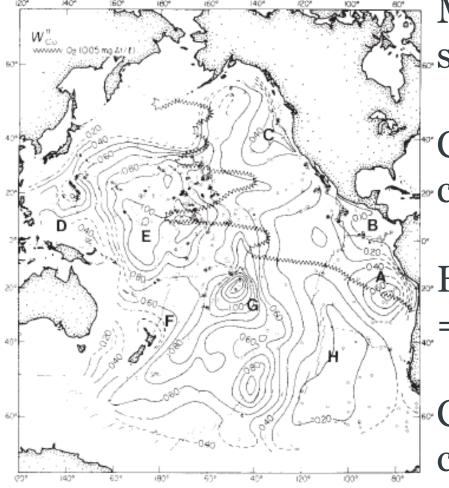
Pelagic clay

Calvert and Cronan, 1978 ₂

Mn nodule accumulation rates

- Mn nodules grow at mm Ma⁻¹
- Enriched in Mn, Fe, Cu, Ni, Co and REE
- Deep sea sediments accumulate at m Ma⁻¹
- How do the nodules remain at the sediment surface?
- Are growth rates underestimated? Are accumulation rates variable? Do burrowing organisms move nodules to the surface? Do bottom currents winnow the sediments?

Cobalt in Mn crusts



Mn crusts accumulate on hard substrates exposed on seafloor

Co content negatively correlates with growth rate

High Co accumulation
= very slow crust growth

Co chronometer provides crust growth rates

Manheim and Lane-Bostwick, 1988



Are deep sea mineral deposits a viable resource?

Deep sea mineral resources

- Nautilus Minerals Inc are developing a production system to extract copper and gold from a relict hydrothermal deposit offshore Papua New Guinea in ~1550m water depth
- The extreme depths and location in International Waters mean that mining of Mn nodules, crusts and REE enriched sediments is logistically extremely challenging and unlikely to be developed in the next few decades

Summary

- Seafloor hydrothermal deposits can be substantial in size (several million tonnes of sulfide)
- Low temperature alteration of deposits generates significant metal enrichment (up to high grade ore)
- Hydrothermal plumes are rich in iron oxides that scavenge metals out of seawater and deposit them at the seafloor (significant deposits of REE)
- At extremely low sediment accumulation rates, minerals form at the seafloor with large metal enrichment (Mn nodules and crusts)

Find out more:

- <u>http://www.noc.soton.ac.uk/chess/</u>
- <u>http://www.whoi.edu/workshops/deepseamining/</u>
- Kato, Y. et al, Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements, Nature Geoscience, doi: 10.1038/NGEO1185.
- http://www.nautilusminerals.com/s/Home.asp
- <u>http://www.geotraces.org</u>



Questions?