14 Chemical extraction of useful substances from the sea
Outline

1. Salt
2. Evaporation of seawater
3. Rock salt
4. Magnesium
5. Bromine
6. Gold
7. Water
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Salt requirement of Tikal

8 g per person per day \( \times \) 45,000 people \( \rightarrow \) 130 t yr\(^{-1}\)

**salary**: \( \leftarrow \) *salarium argentum* ("silver salt")

Throughout history, the most important chemical substance extracted from the sea has been common salt.
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Concentrations of salts in seawater
Evaporation of seawater

Precipitates from residual bitterns: MgSO₄, KCl, NaBr, MgCl₂, many others

CaCO₃ (0.1 g); CaSO₄ · 2H₂O (1.7 g); NaCl (21 g); bitterns
Separation of NaCl
Global production of salt

$$290 \times 10^6 \text{ t yr}^{-1}$$

20 - 30% from evaporation of seawater

The rest from the mining of salt deposits

A Mexican company (330 km$^2$ wide salterns):
7,500,000 t yr$^{-1}$ $\rightarrow$ 20,000 t day$^{-1}$
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Evaporative concentration of seawater

- Mediterranean and Red seas
- No return flow
- Sequential deposit of salts?
Strassfurt deposit

Late Permian (∼ 225 × 10^6 years)

600 m of salt ← 35,000 m of seawater

∴ The deposit must have resulted from repeated flooding and evaporation of a shallow sea.
Diverse salt deposits

This sequence ($\text{CaCO}_3$, gypsum, $\text{NaCl}$, bitterns), observed since the Cambrian.

→ The ratios of the major ions in seawater have been roughly the same throughout the last 600 million years.
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Extraction of magnesium from seawater

Global production of Mg: $7 \times 10^6$ t yr$^{-1}$ (in 2011)

5 - 6% from seawater

It is often cheaper to produce magnesium from various terrestrial brines or from certain minerals.

1. $\text{CaCO}_3 + \text{heat (1300}^\circ\text{C)} \rightarrow \text{CaO} + \text{CO}_2 \uparrow$
2. $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
3. $\text{Ca(OH)}_2 + \text{Mg}^{2+} \rightarrow \text{Mg(OH)}_2 \downarrow + \text{Ca}^{2+}$
5. $\text{Mg(OH)}_2 + \text{heat} \rightarrow \text{MgO} + \text{H}_2\text{O} \uparrow$

6. Dissolution of $\text{Mg(OH)}_2$ with HCl to make $\text{MgCl}_2$ solution; Mg metal by electrolysis
Global production of bromine: $0.66 \times 10^6$ t yr$^{-1}$ (in 2011)

In the USA, it has been found more economical to obtain bromine from certain salt deposits in Arkansas that are rich in the residual products from the ancient crystallization of salt from seawater.
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Gold concentrations (per ton of seawater)

1872: 65 mg (Sonstadt)
1900: 6 mg (Arrhenius)

During the first four decades of the twentieth century, there were at least 50 patents issued in various countries for methods to extract gold from seawater.

1920: 0.004 mg (Haber)
1950s: 0.09 mg (1/100 cents) from 15 ton of seawater (Dow Chemical Co.) → It costed $50,000!
1990: 50 fmol kg$^{-1}$ ($\approx 10^{-5}$ mg per ton; Falkner and Edmond) ↓

14,000 tons in the ocean < 30,000 tons in the central banks
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Water production from seawater

Global production: $60 \times 10^6$ ton per day

$0.60 - $0.80 per m$^3$ in USA

Distillation and condensation

**Reverse osmosis (RO)** procedure uses somewhat less energy than the distilling processes.
Hydrostatic head as a measure of osmotic pressure

\[ \Pi = cRT \quad \text{Eq (6.3)} \]

\( \Pi \): the pressure;  
\( c \): the concentration in moles per liter;  
\( R \): the gas constant  
\( T \): the absolute temperature in kelvins.

1 mol \( \rightarrow \) 24.6 atm  
35\% \ (1.15 \text{ mol}) \rightarrow 28 \text{ atm}
Key elements of a desalination system

The reverse osmosis (RO) process uses semipermeable membranes and a driving force of hydraulic pressure to remove dissolved solids from brackish water or seawater.