



Idaho National Laboratory

Nuclear Production of Hydrogen and Transportation Fuels

Dr. J. Stephen Herring

Laboratory Fellow

Deputy Director

Nuclear Science and Engineering Division

Electric Power and Energy Systems Seminar

Electrical Engineering

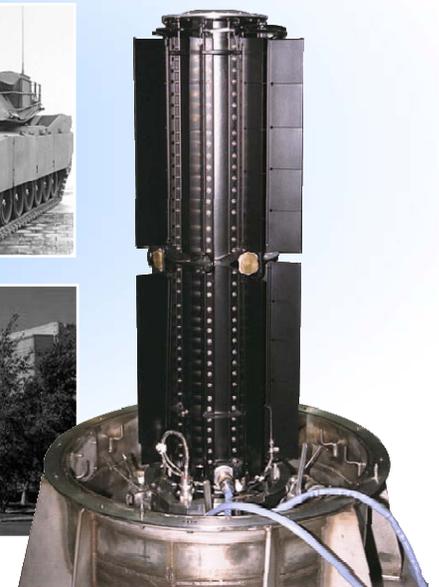
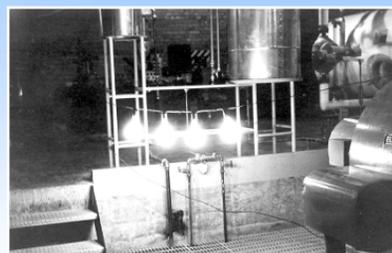
and Computer Science Department

Iowa State University

February 15, 2011

INL Overview Historic Contributions

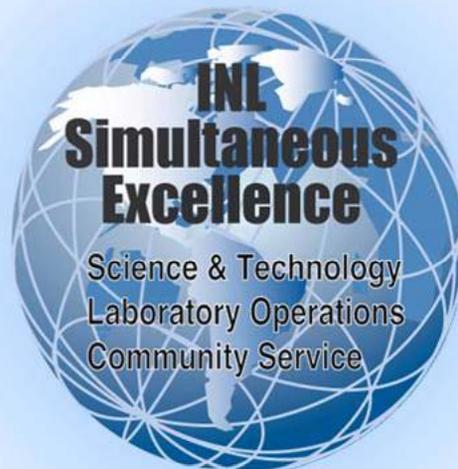
- **Proof of breeder reactor concept**
- **Development of Navy nuclear propulsion systems/operator training**
- **Design and construction of 52 nuclear reactors**
- **Production of key medical and industrial isotopes**
- **Nuclear reactor safety code development**
- **Leadership of DOE hydropower and geothermal programs**
- **Hybrid and electric vehicle testing**
- **Armor production**
- **NASA program support**



Idaho National Laboratory — Our Present

LABORATORY

Battelle
Laboratory Expertise



Nuclear Operations



the babcock & wilcox company

Infrastructure Management



Washington Division

Industry Connection



National University Consortia



Massachusetts Institute of Technology

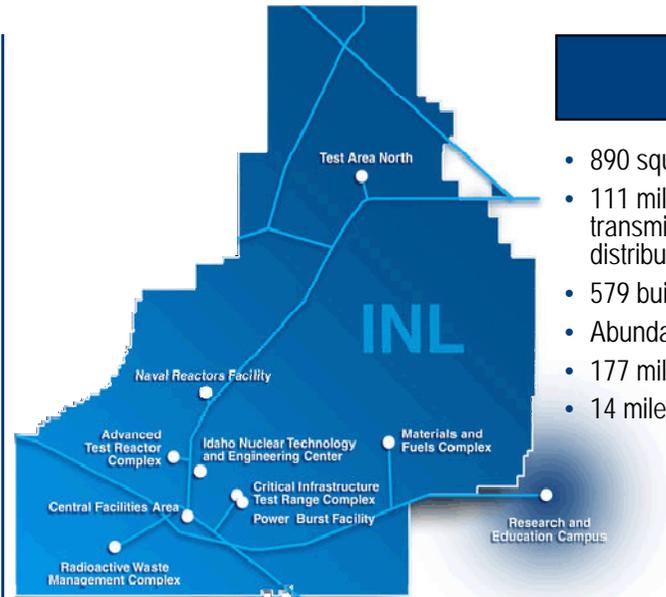


University of Idaho



University of Idaho

SITE



- 890 square miles
- 111 miles of electrical transmission and distribution lines
- 579 buildings
- Abundant water
- 177 miles of paved roads
- 14 miles of railroad lines



4400 Employees
Business Volume \$800M



1675 Employees
Business Volume \$365M

Naval Reactors Facility

1450 Employees



850 Employees
Business Volume \$124M

Idaho National Laboratory — The National Nuclear Laboratory

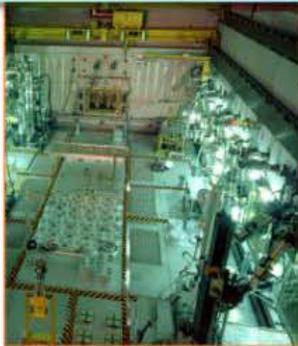
INL's Position Today — Nationally

- **One of only 10 DOE multi-program labs**
- **DOE's designated lead lab for nuclear energy research, development and demonstration**
- **A major contributor in national and homeland security**
- **Regional contributor to clean energy technologies**



Idaho National Laboratory — Vision

Developing world-class Nuclear Energy capabilities



Fostering education, research, industry, government and international collaborations to produce the needed investment, programs and expertise



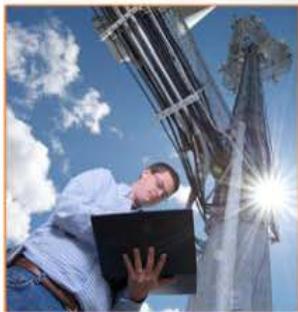
CAES

Center for Advanced Energy Studies



Preeminent Internationally-Recognized Nuclear Energy RDD&D Laboratory

INL Wireless
TEST BED



Major center for National and Homeland Security technology RDD&D

Lead clean energy systems RDD&D laboratory and a regional resource

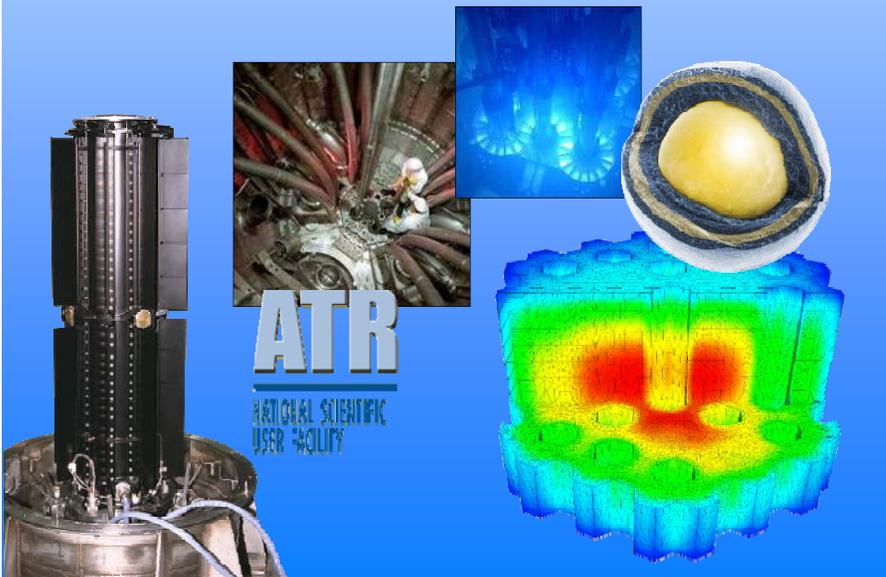
The nuclear energy mission is the reason INL exists

Research Programs of National Importance

Nuclear Energy

- ▶ Advanced Fuel Cycle R&D
- ▶ Next Generation Nuclear Plant (NGNP)
- ▶ ATR National Scientific User Facility
- ▶ Space Nuclear

U.S. National Nuclear Energy Laboratory and an International leader



National & Homeland Security

- ▶ Supervisory Control and Data Acquisition (SCADA) Work
- ▶ Grid Reliability and Security
- ▶ Cyber Security
- ▶ Wireless Communications
- ▶ Nuclear Nonproliferation
- ▶ Armor, Explosive Blast Protection

A leader in critical infrastructure protection and homeland security



Energy & Environment

- ▶ Hybrid Energy Systems
- ▶ Non-traditional Hydrocarbon use
- ▶ Bio-fuels and Synfuels
- ▶ Clean Energy and Water
- ▶ Battery Technology

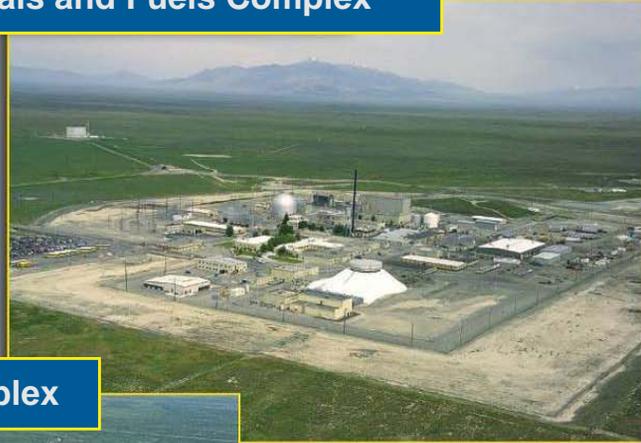
A leader in developing solutions to energy, resources and infrastructure challenges in the State, Region and Nation



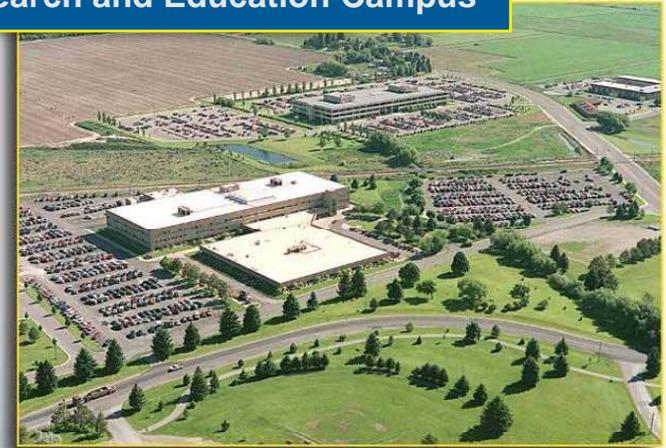
Delivering technologies that benefit our communities, state, region and country

INL's Three Main Facility Areas

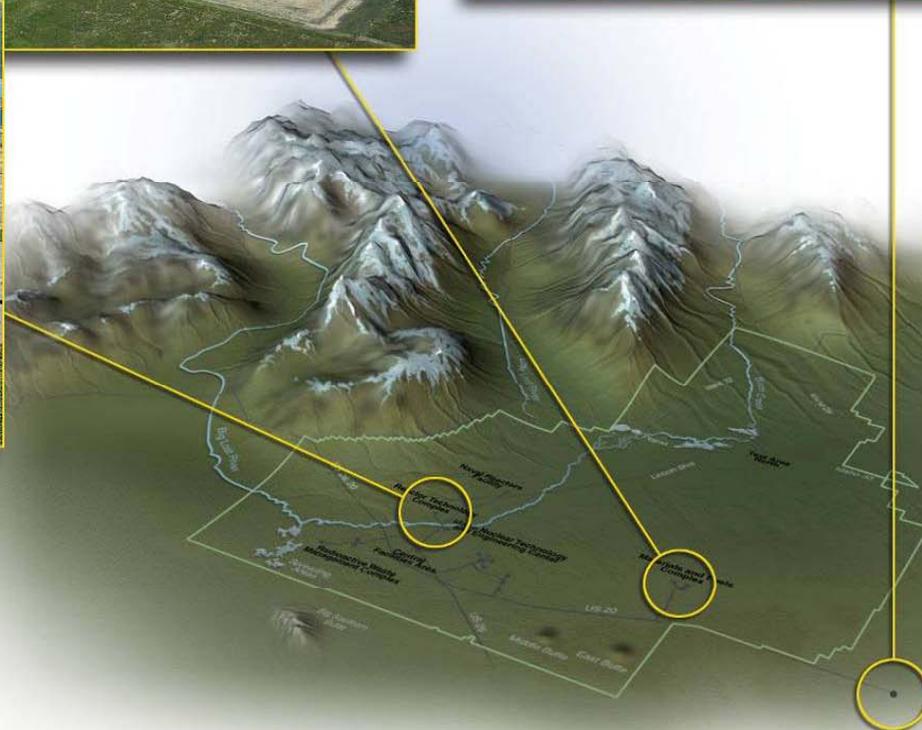
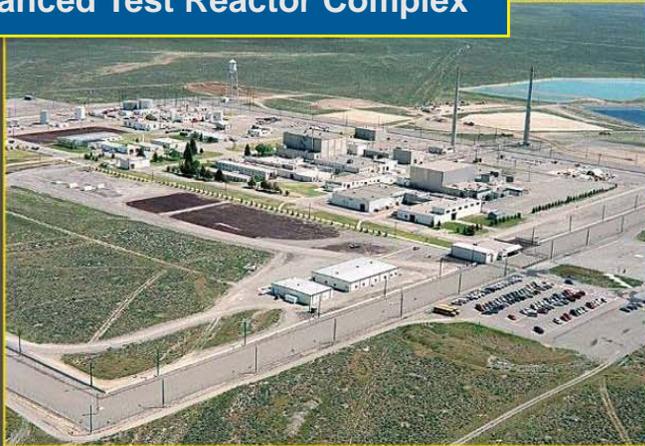
Materials and Fuels Complex



Research and Education Campus



Advanced Test Reactor Complex



Advanced Test Reactor Complex

Key Assets:

- **Advanced Test Reactor**
 - Nation's most versatile test reactor
 - Materials and fuels testing, isotope production
 - National Scientific User Facility
- **STAR**
 - Fusion safety testing

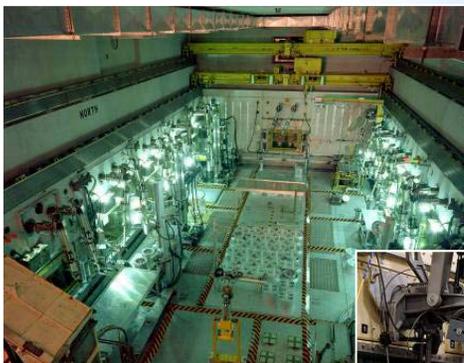


Advanced Test Reactor core

Materials and Fuels Complex

Key Assets:

- **Hot Fuel Examination Facility/Fuel Conditioning Facility**
 - Hot cells for fuel studies
- **Center for Space and Security Power Systems**
 - Assembly and testing of space batteries



Hot Fuel Examination Facility



Space and Security Power Systems Facility

Research and Education Campus

Key Assets:

- **INL Research Center**
 - Multiprogram labs
- **Information Operations Research Center**
 - National and Homeland Security studies



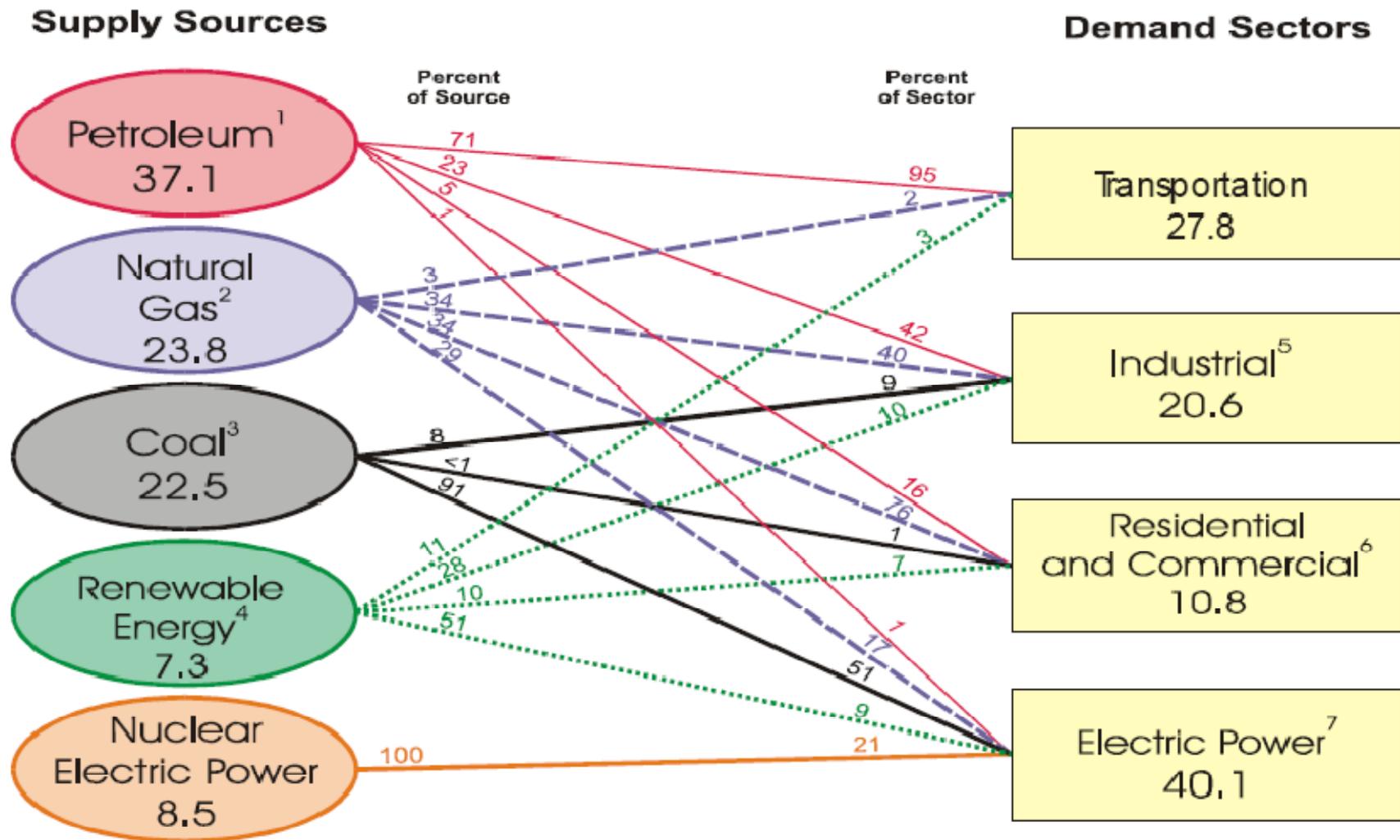
Nuclear hydrogen, high temperature electrolysis



IceStorm supercomputer



Figure 2.0 Primary Energy Consumption by Source and Sector, 2008
(Quadrillion Btu)



¹ Does not include the fuel ethanol portion of motor gasoline—fuel ethanol is included in "Renewable Energy."

² Excludes supplemental gaseous fuels.

³ Includes less than 0.1 quadrillion Btu of coal coke net imports.

⁴ Conventional hydroelectric power, geothermal, solar/PV, wind, and biomass.

⁵ Includes industrial combined-heat-and-power (CHP) and industrial electricity-only plants.

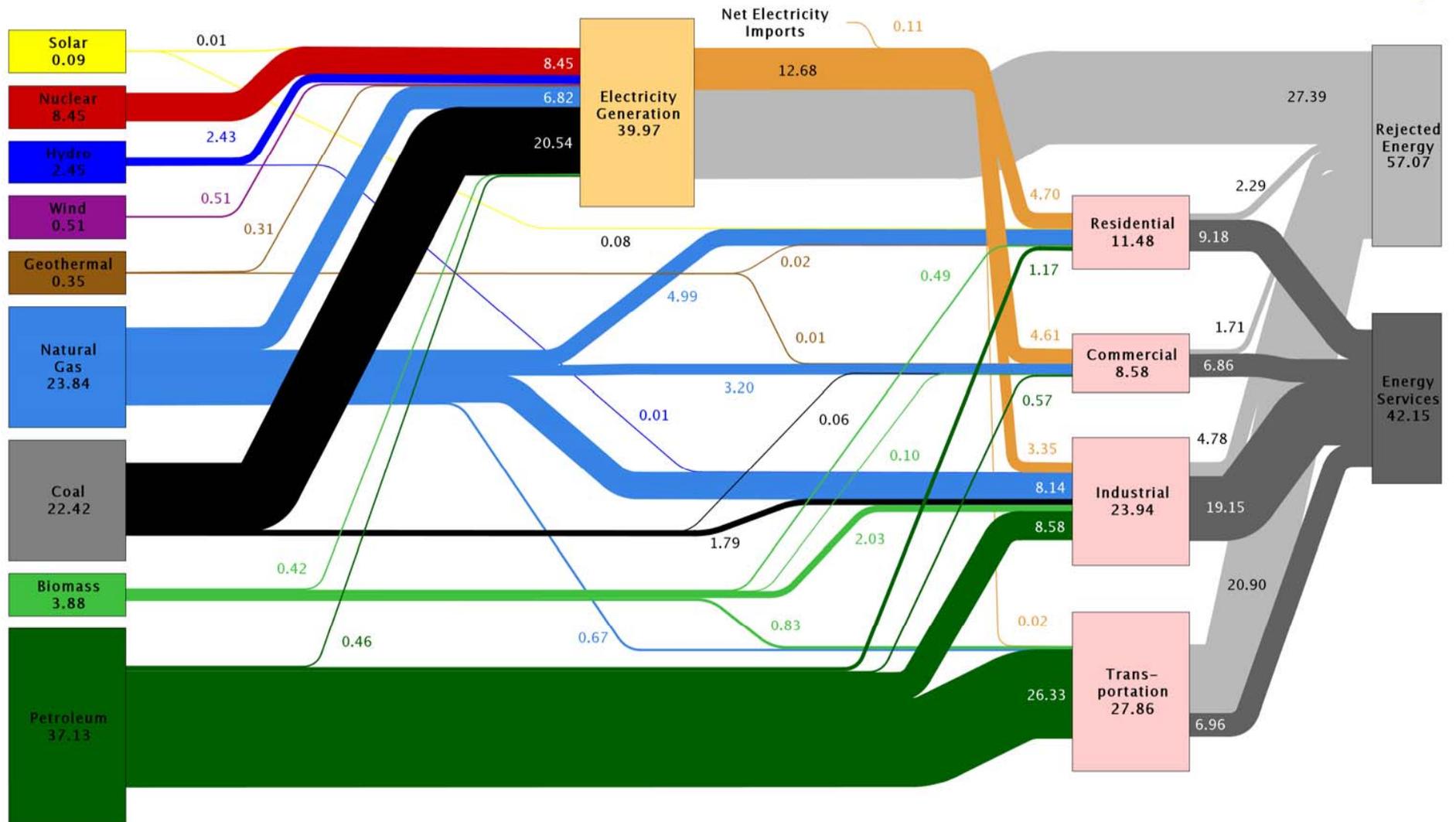
⁶ Includes commercial combined-heat-and-power (CHP) and commercial electricity-only plants.

⁷ Electricity-only and combined-heat-and-power (CHP) plants whose primary business is to sell electricity, or electricity and heat, to the public.

Note: Sum of components may not equal 100 percent due to independent rounding.

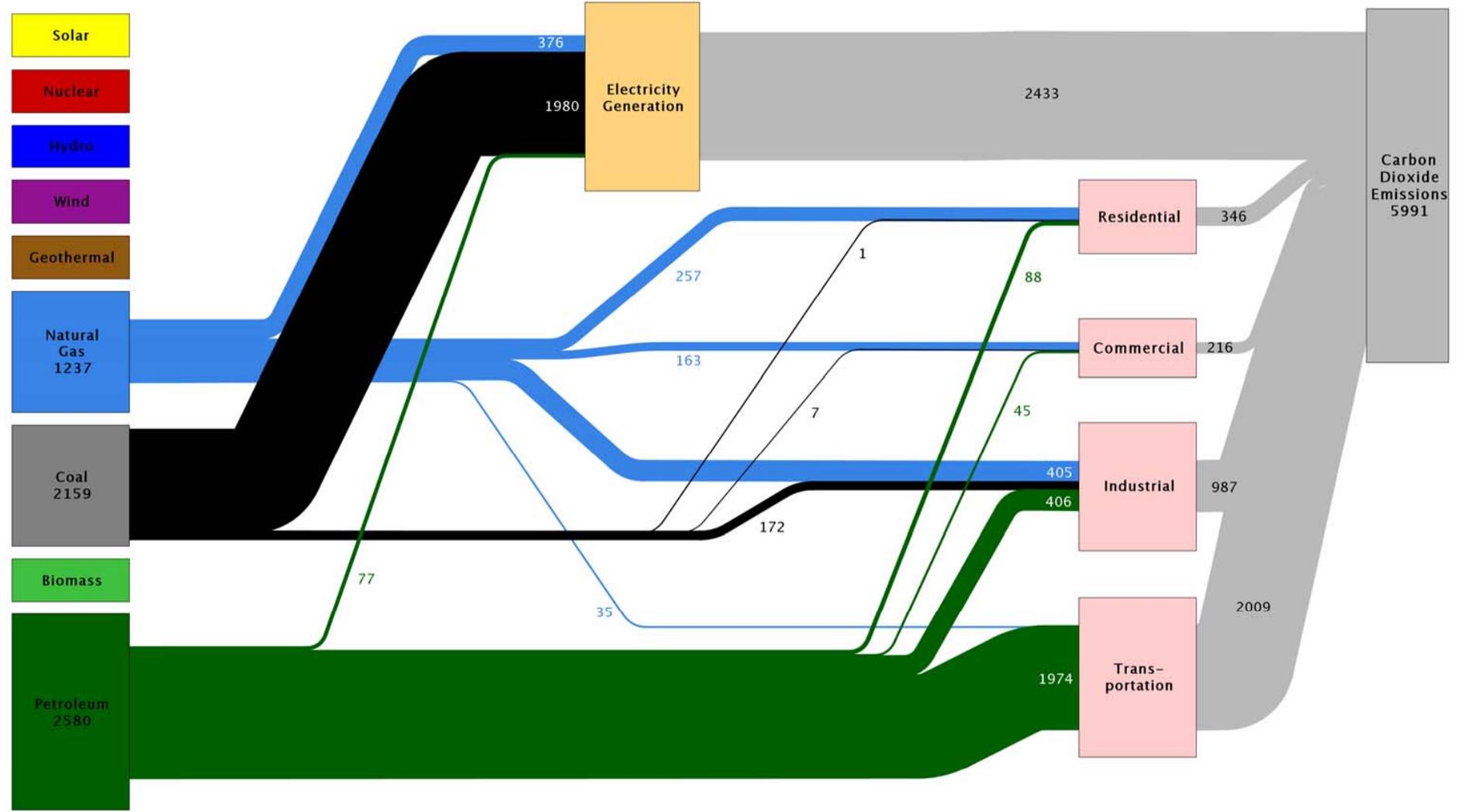
Sources: Energy Information Administration, *Annual Energy Review 2008*, Tables 1.3, 2.1b-2.1f, 10.3, and 10.4.

Estimated U.S. Energy Use in 2008: ~99.2 Quads



Source: LLNL 2009. Data is based on DOE/EIA-0384(2008), June 2009. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports flows for non-thermal resources (i.e., hydro, wind and solar) in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

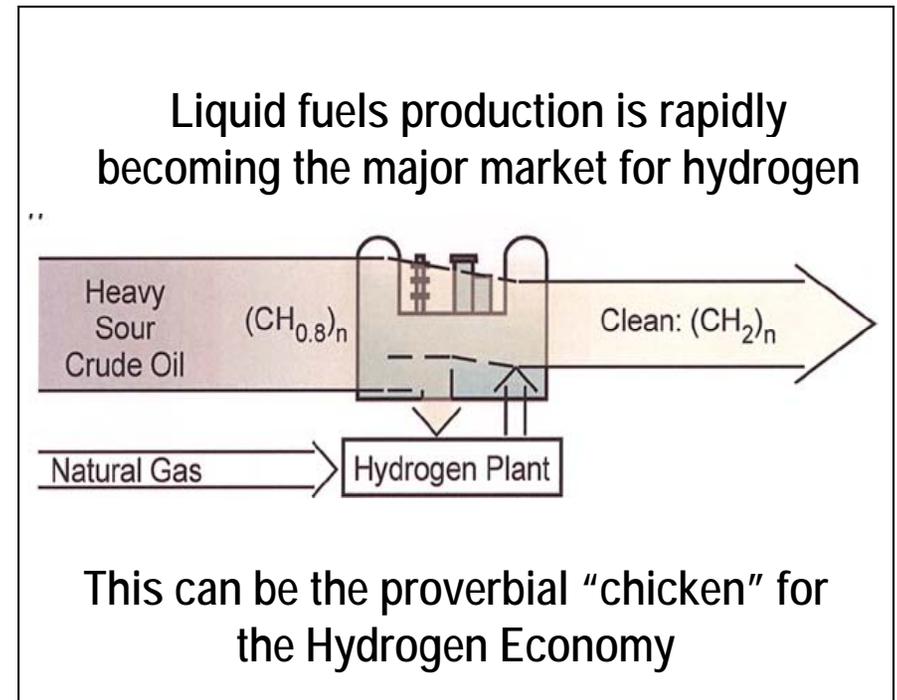
Estimated U.S. Carbon Dioxide Emissions in 2007: ~5991 Million Metric Tons



Source: LLNL 2009. Data is based on DOE/EIA-0384(2008), June 2009. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Carbon embodied in industrial and commercial products such as plastics is not shown. The flow of petroleum to electricity production includes both petroleum fuels and the plastics component of municipal solid waste. The combustion of biologically derived fuels is assumed to have zero net carbon emissions - lifecycle emissions associated with biofuels are accounted for in the Industrial and Commercial sectors. Totals may not equal sum of components due to independent rounding. LLNL-MI-411167

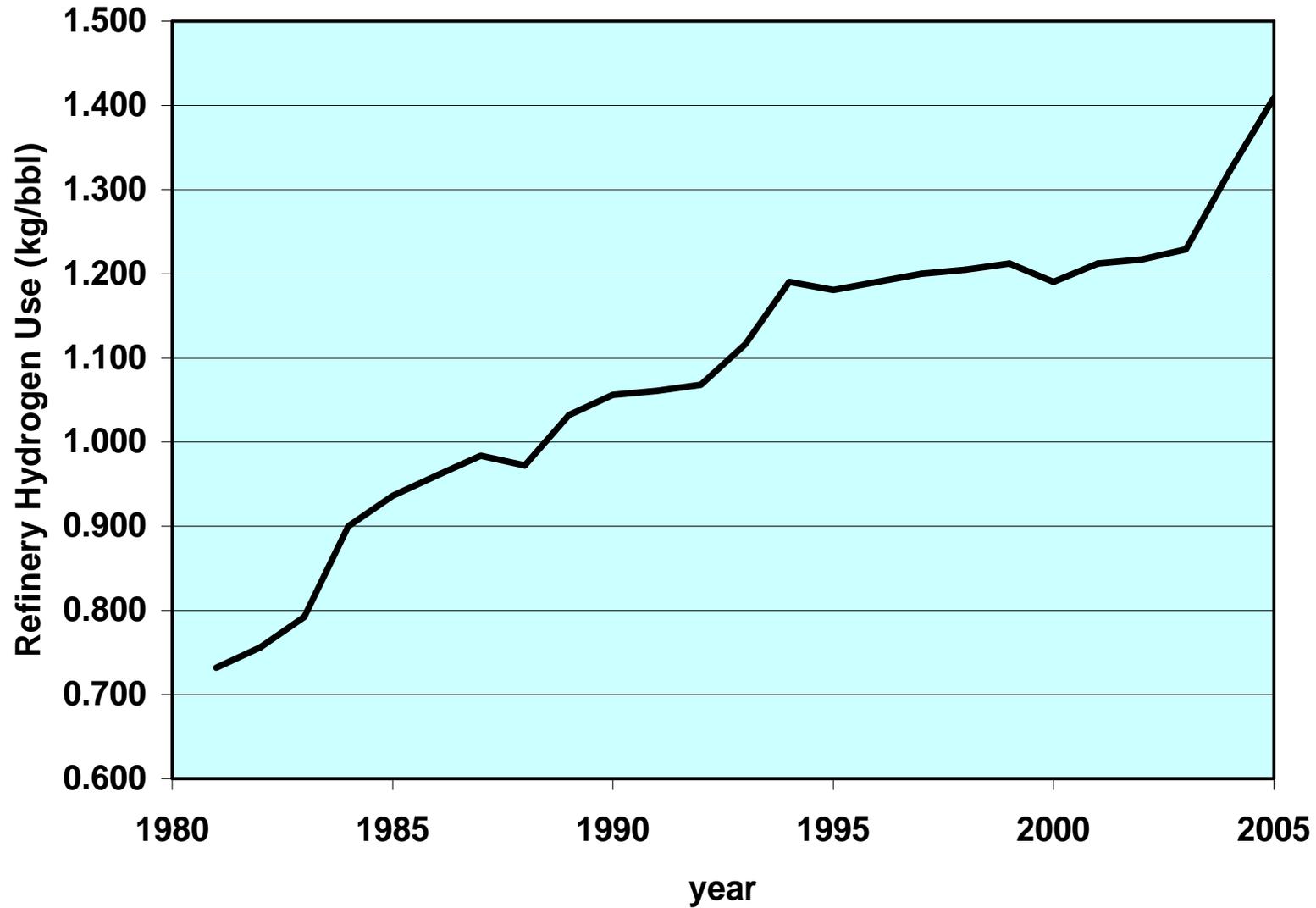
Present US Hydrogen Consumption

- Petroleum refining
 - Sulfur removal
 - Opening of Benzene rings
 - Breaking of long-chain hydrocarbons
 - trends will continue in the future, e.g. Athabasca oil sands
- Anhydrous Ammonia Production for fertilizer
- Chemical Industry
- 2005 US consumption: 13 million tons H_2 /yr
 - 95% produced by steam reforming of natural gas (8 % of US natural gas use)
 - Releases 80 million tons CO_2 /yr



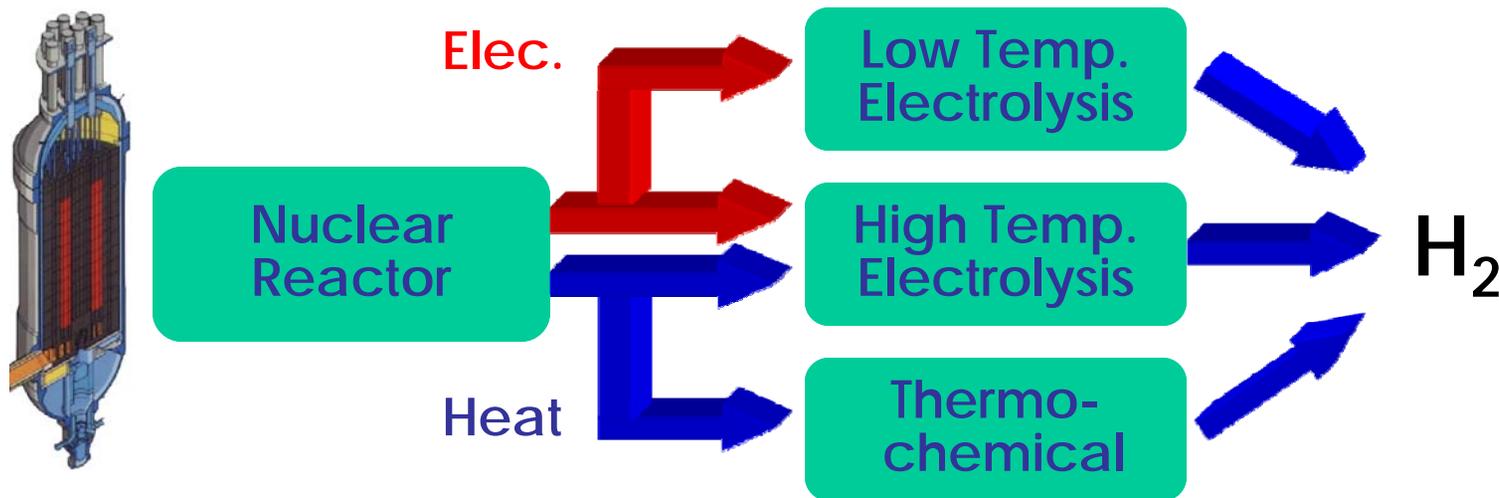
- Replacing present US transportation fuels (gasoline, diesel, jet fuel) with hydrogen would require a 17-fold increase in our hydrogen production.
 - Would consume >100% of our natural gas supply, or
 - Would require ~500 1000-MWe power plants to provide the energy for water splitting

US Refinery Hydrogen Consumption, kg/Barrel Crude



H₂ can be manufactured cleanly by using nuclear energy for water-splitting

- A Hydrogen Economy only makes sense if the H₂ is produced from non-fossil, non-greenhouse gas-emitting, sustainable sources

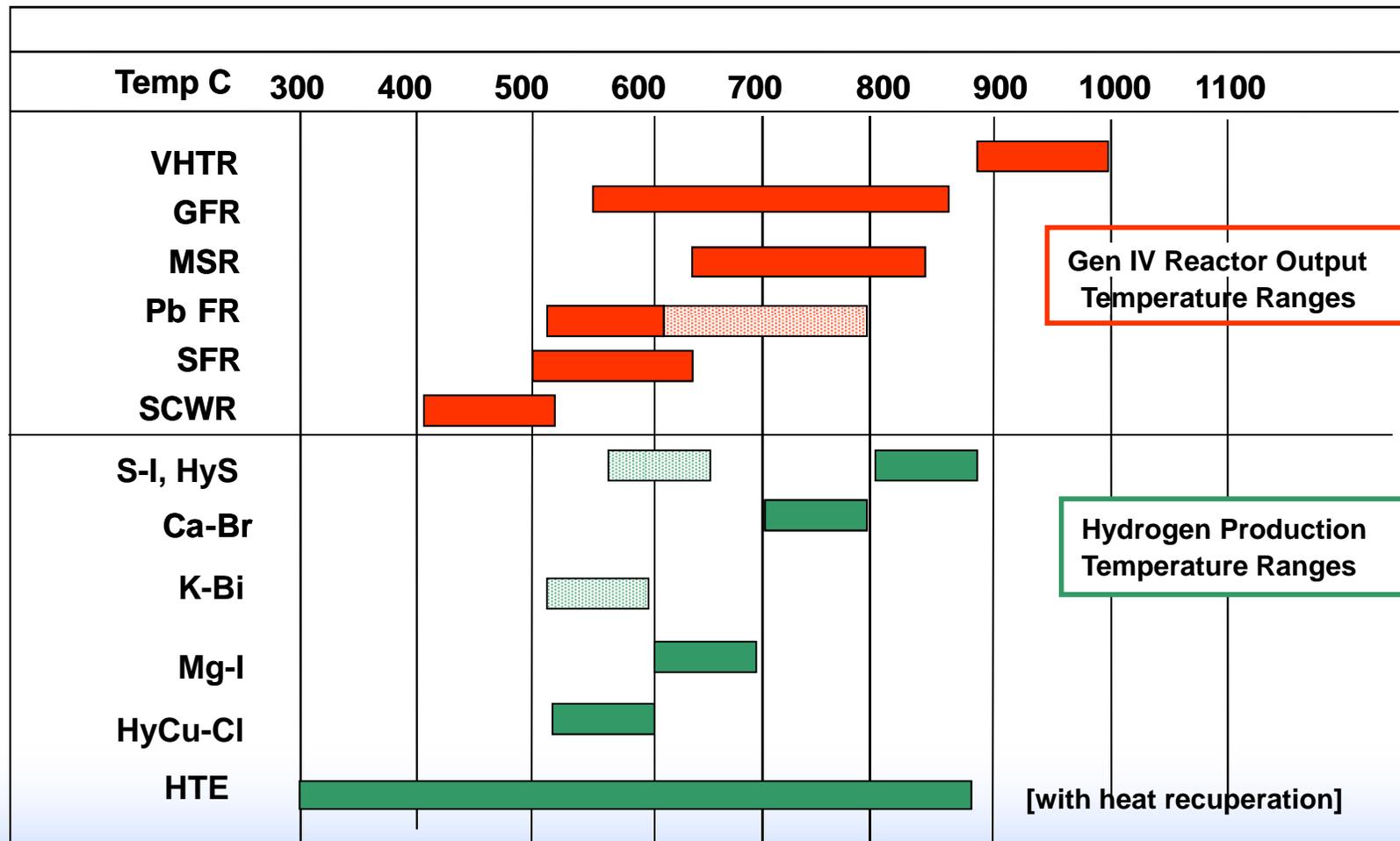


All of these methods split water into hydrogen and oxygen.

Though the heat or electricity to split the water comes from a reactor, the hydrogen is not radioactive.

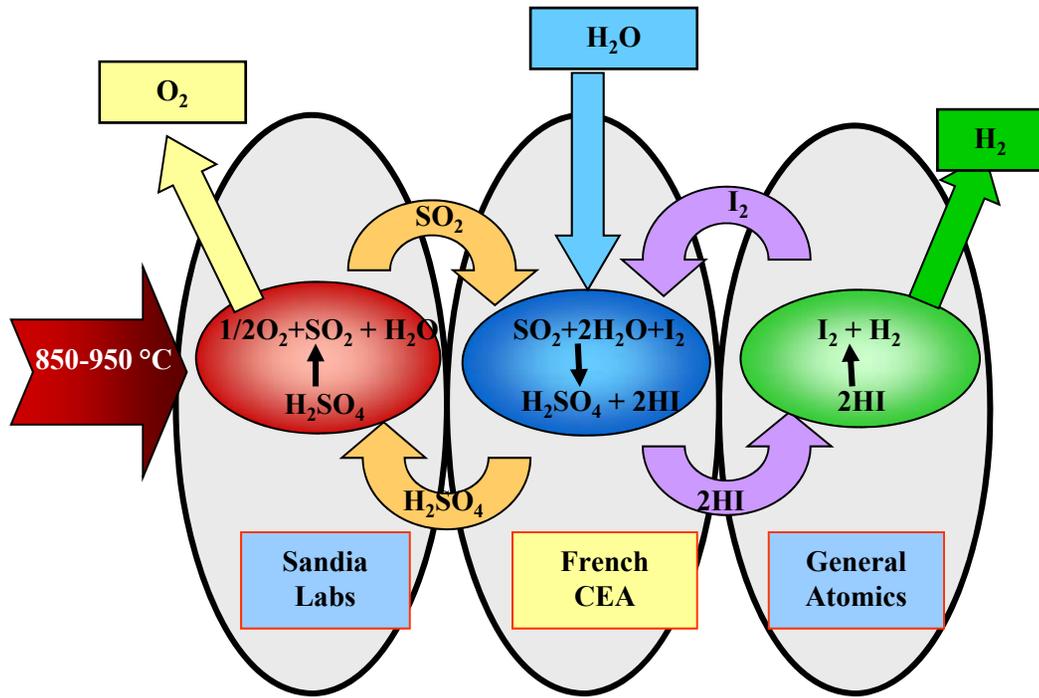
Generation IV Energy Conversion

- Electrical generation - *Gen IV Energy Conversion Program*
- Hydrogen production - *Nuclear Hydrogen Initiative (NHI)*



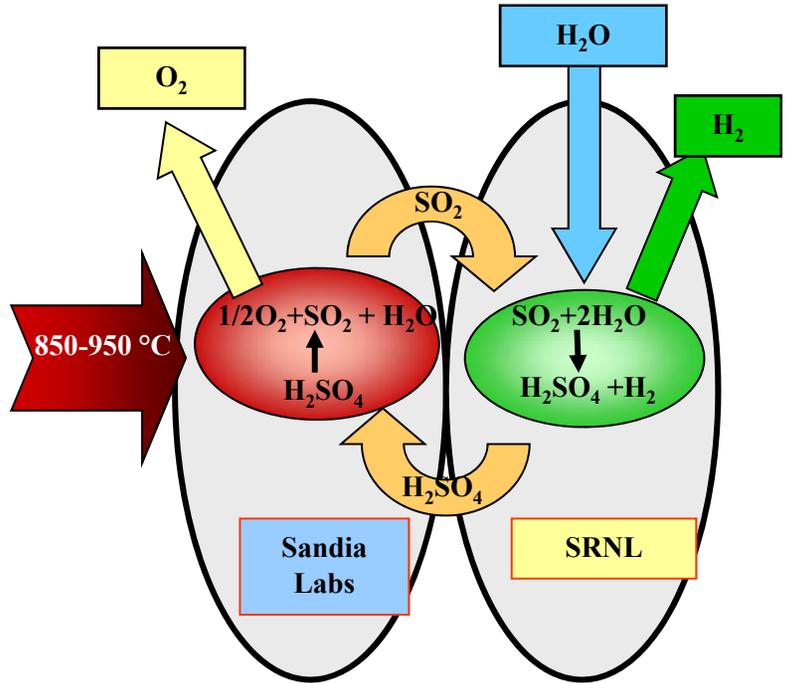
Sulfur Thermochemical Cycles

TC cycles require high temperatures, extensive thermal management, and high temperature, corrosion resistant materials



Sulfur Iodine

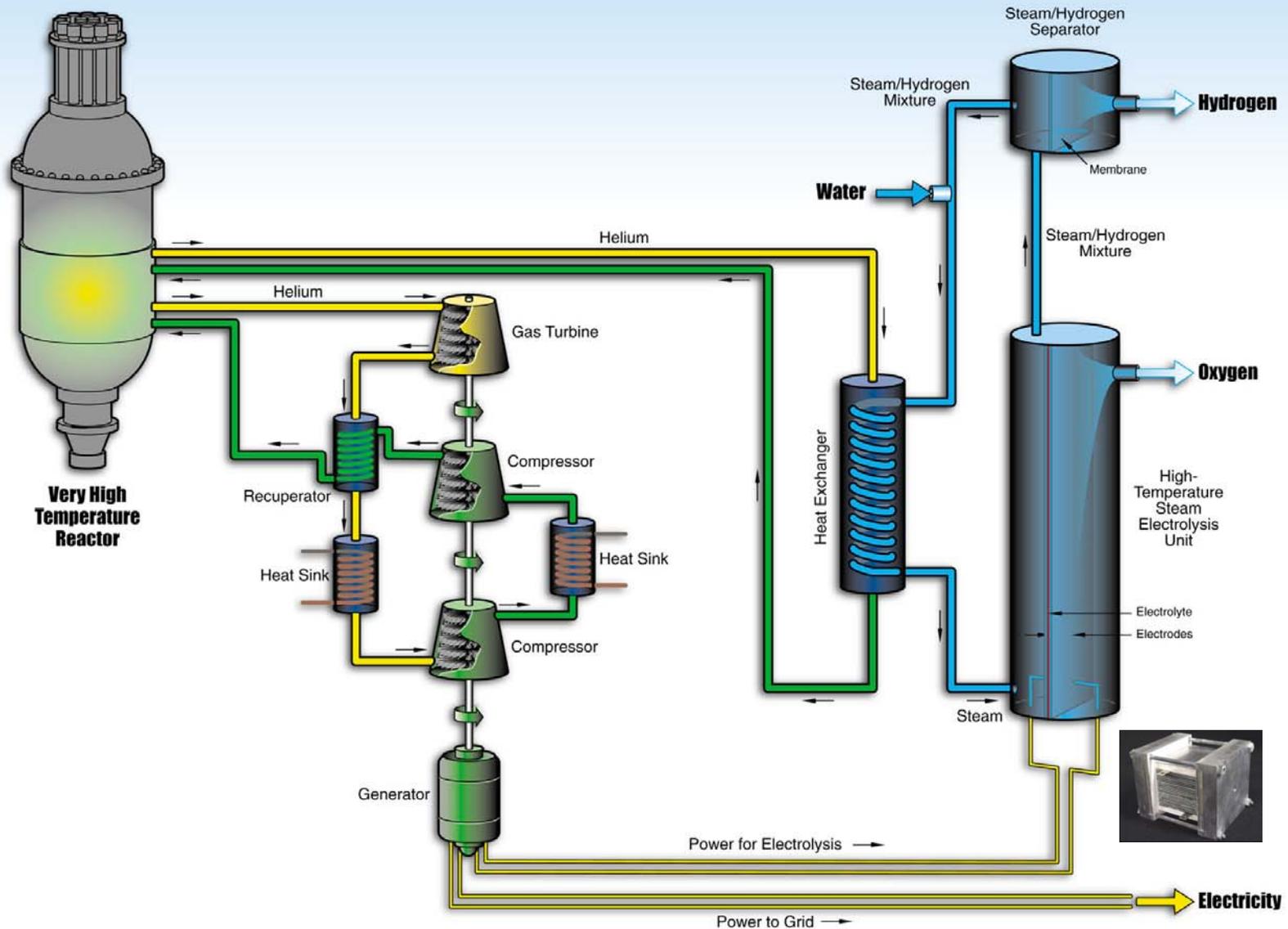
- (1) $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2$
- (2) $2\text{HI} \rightarrow \text{I}_2 + \text{H}_2$
- (3) $2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$



Hybrid-Sulfur

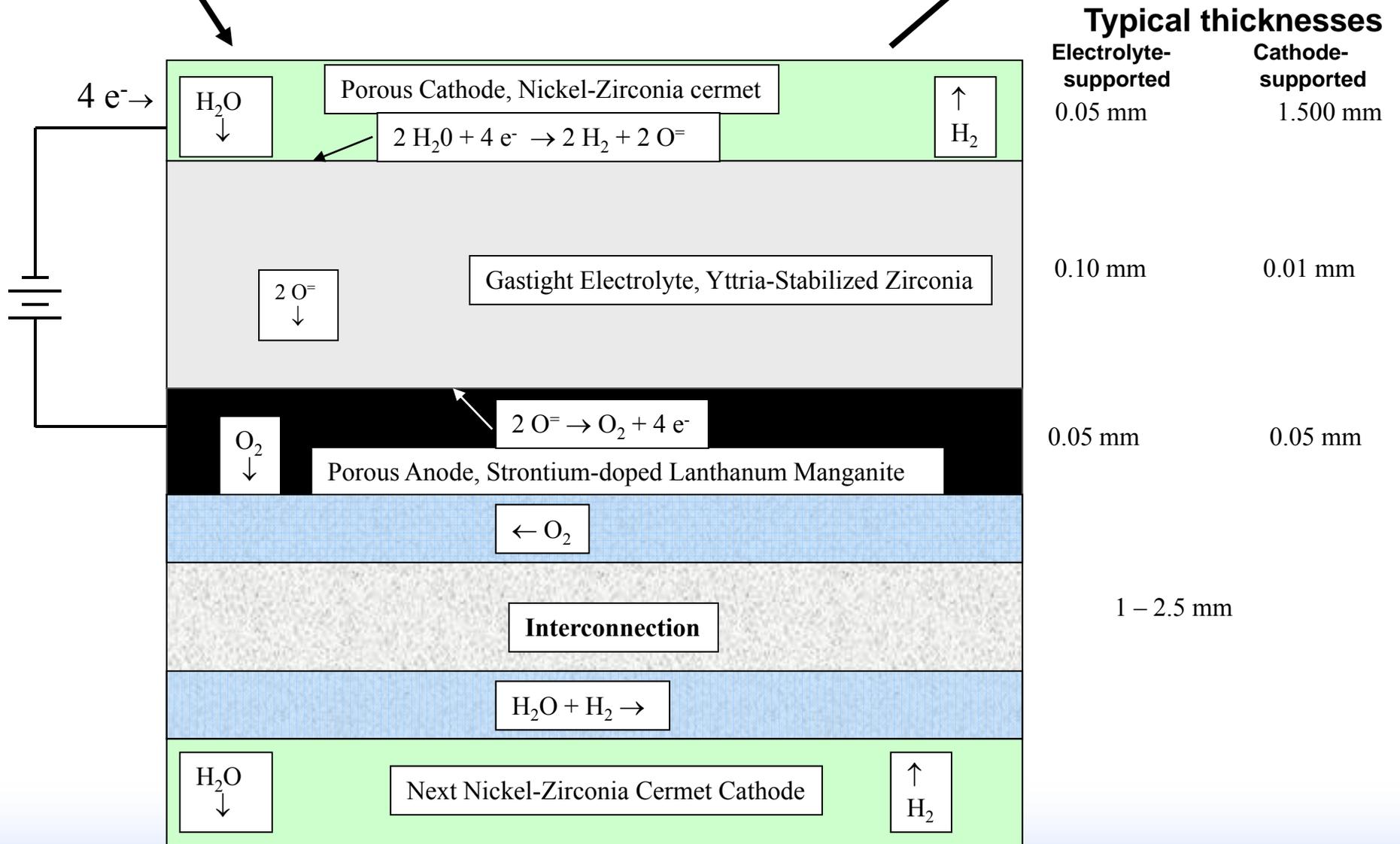
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- (2) $2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2$

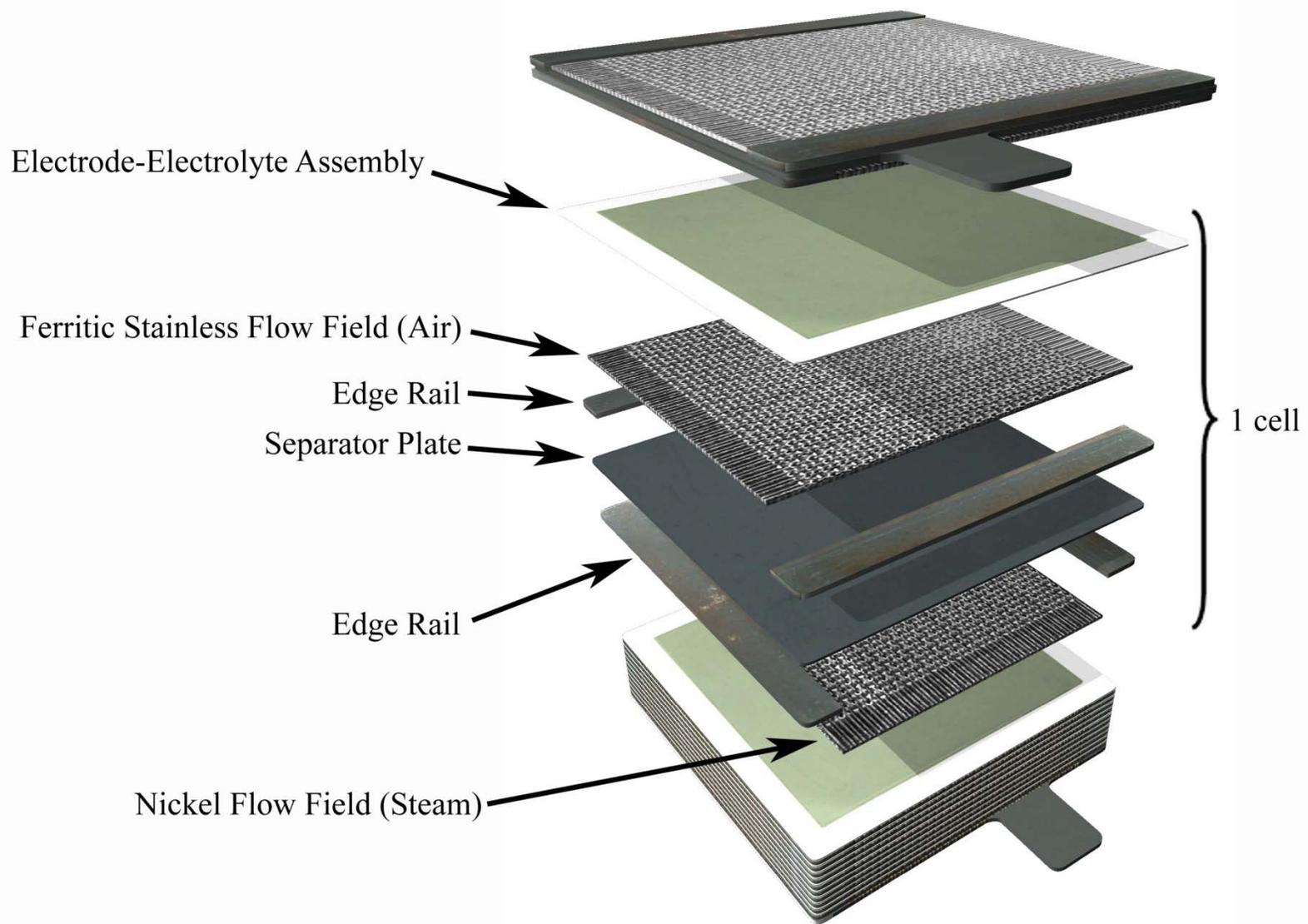
High Temperature Electrolysis Plant



90 v/o H₂O + 10 v/o H₂

25 v/o H₂O + 75 v/o H₂





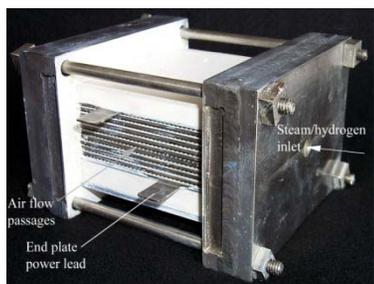
High-Temperature Electrolysis (HTE) research and development activities at INL

Integrated Laboratory Scale Facility

Button cell



Short stacks

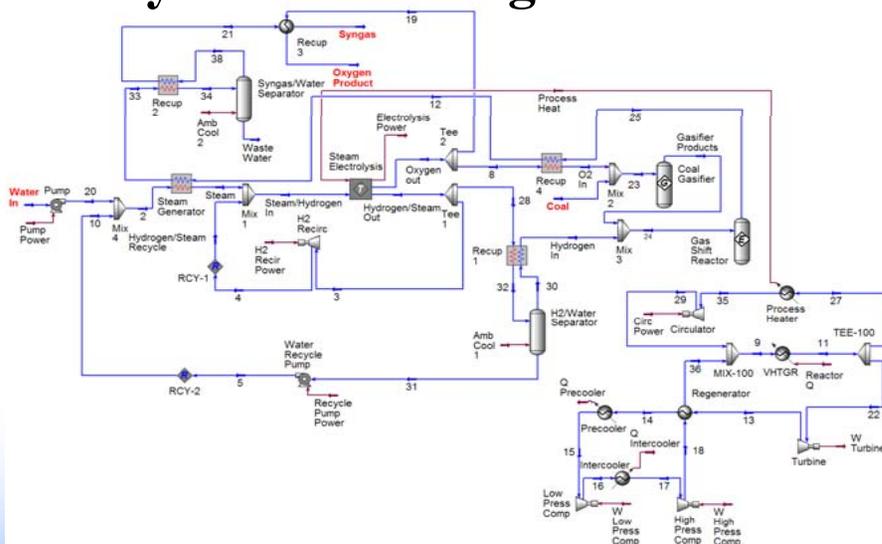
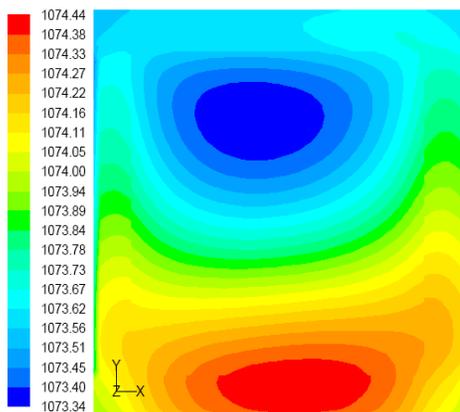


70 NL/hr

HTE research laboratory



CFD and system modeling



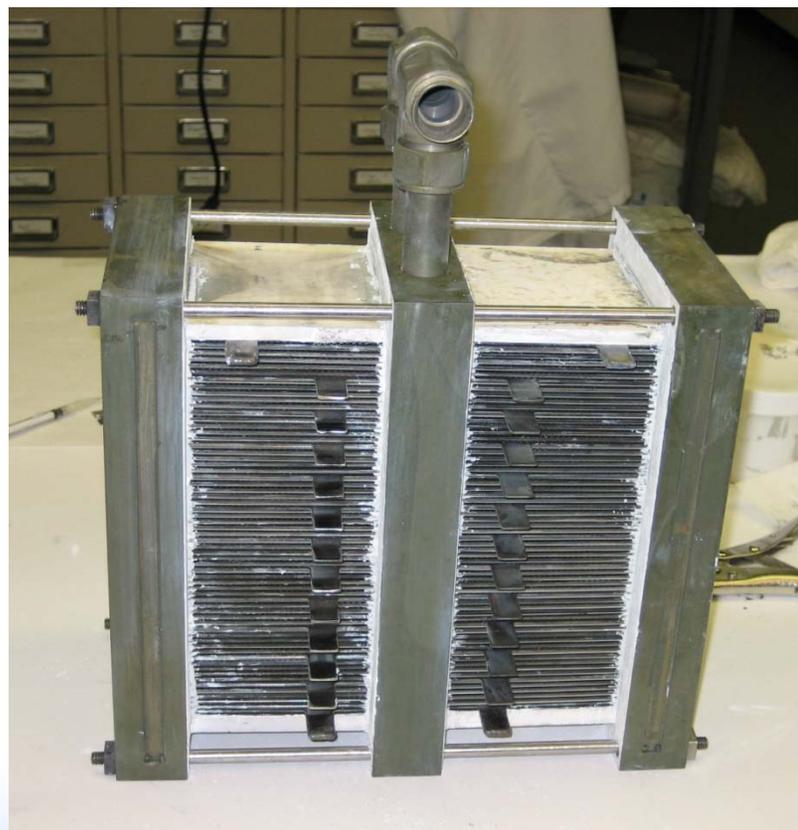
INL has demonstrated H₂ production rates up to 5.6 Nm³/hr in the ILS facility

**25-cell stack used in
1000-hour test
Jan. 4 – Feb. 16, 2006**



**2 x 60-cell stacks
tested at
Ceramatec, SLC**

Initial rate: 1.2 Nm³ H₂/hr
final: 0.65 Nm³ H₂/hr
2040 hours, ended 9-22-06
>800 hrs in co-electrolysis



Transportation fuels are becoming our highest priced energy carriers

- **Electricity:**

$$\text{\$0.10 /kW}_e\text{-hour} = \text{\$27.78/GJ}_{\text{electric}}$$

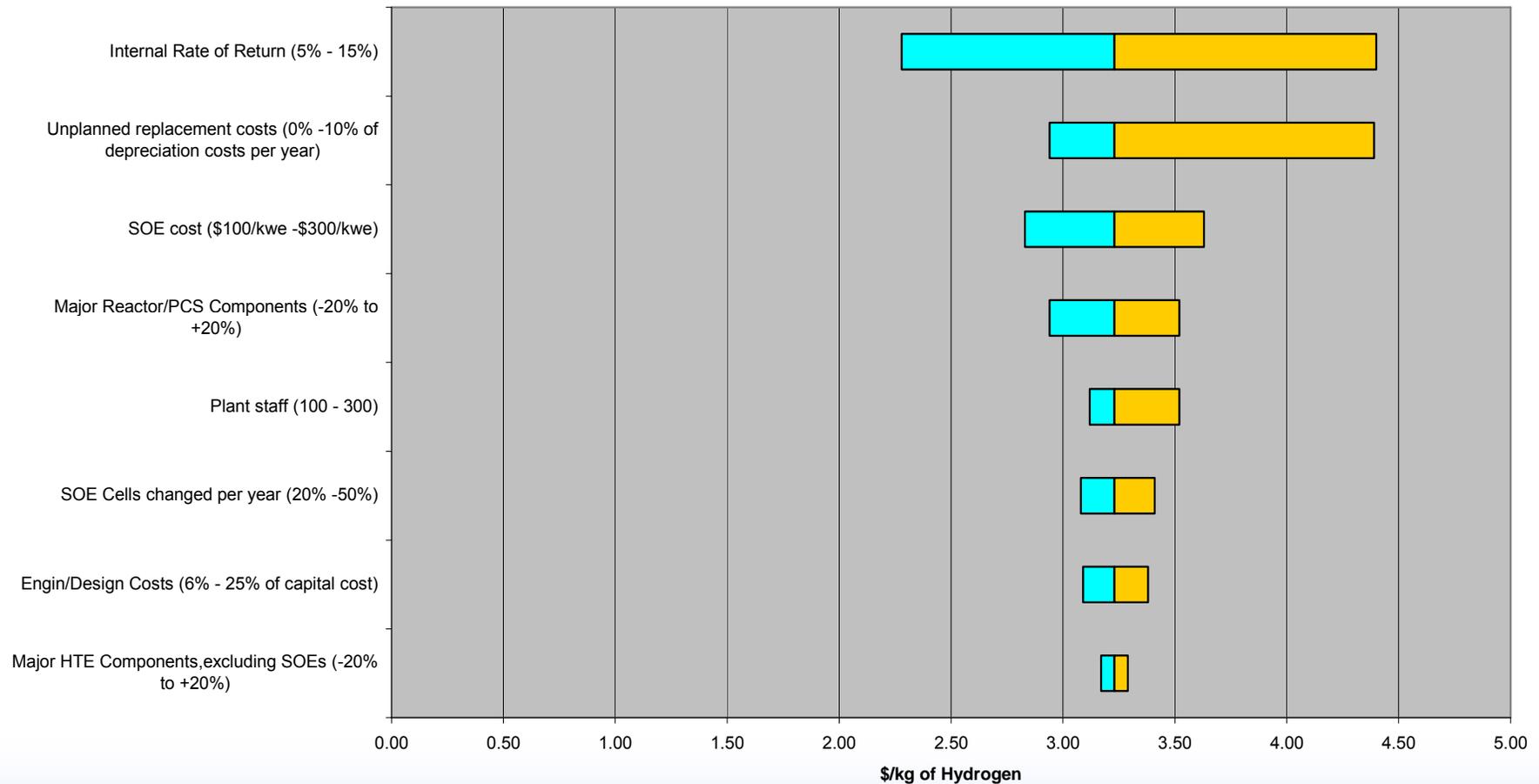
- **Diesel fuel:**

$$\begin{aligned} \text{\$4.00/gallon}^*, & \text{ (139,000 BTU/gallon)} \\ & = \text{\$27.28/GJ}_{\text{thermal}} \end{aligned}$$

* Federal tax: \$0.224/gallon
Average state tax: \$0.22/gallon

VHTR/HTE Economic Sensitivity Analysis

(For plant gate cost ~\$3.23/kg hydrogen and 10% internal rate of return)



Assembled ILS Components



ILS Module Installation



Inevitable Comparison:

Liquid hydrocarbons are very good fuels for transportation

- Liquid over range of ambient temperatures
- Pumpable: gas pump: 20 liters/min = 11 MW_{th}
- Energy dense: 34 MJ_{th}/liter at 0.1 MPa
 - H₂ gas: 9.9 MJ_{th}/liter at 80 MPa,
 - H₂ 120 MJ_{th}/kg, gasoline: 40 MJ_{th}/kg
- Storable: little loss, explosion hazards understood
- Transportable by pipeline: 0.91 m oil pipeline: 70 GW_{th}

Hydrogen will be used primarily to enhance gasoline, diesel and jet fuel production until the on-board storage problem can be solved.

Co-Electrolysis

- Primarily a “proof-of-principle” research project
- Investigate the feasibility of producing syngas

Syngas

2H_2 and CO

- using high-temperature **co-electrolysis** of H_2O and CO_2



- while taking advantage of solid oxide fuel cell technology.

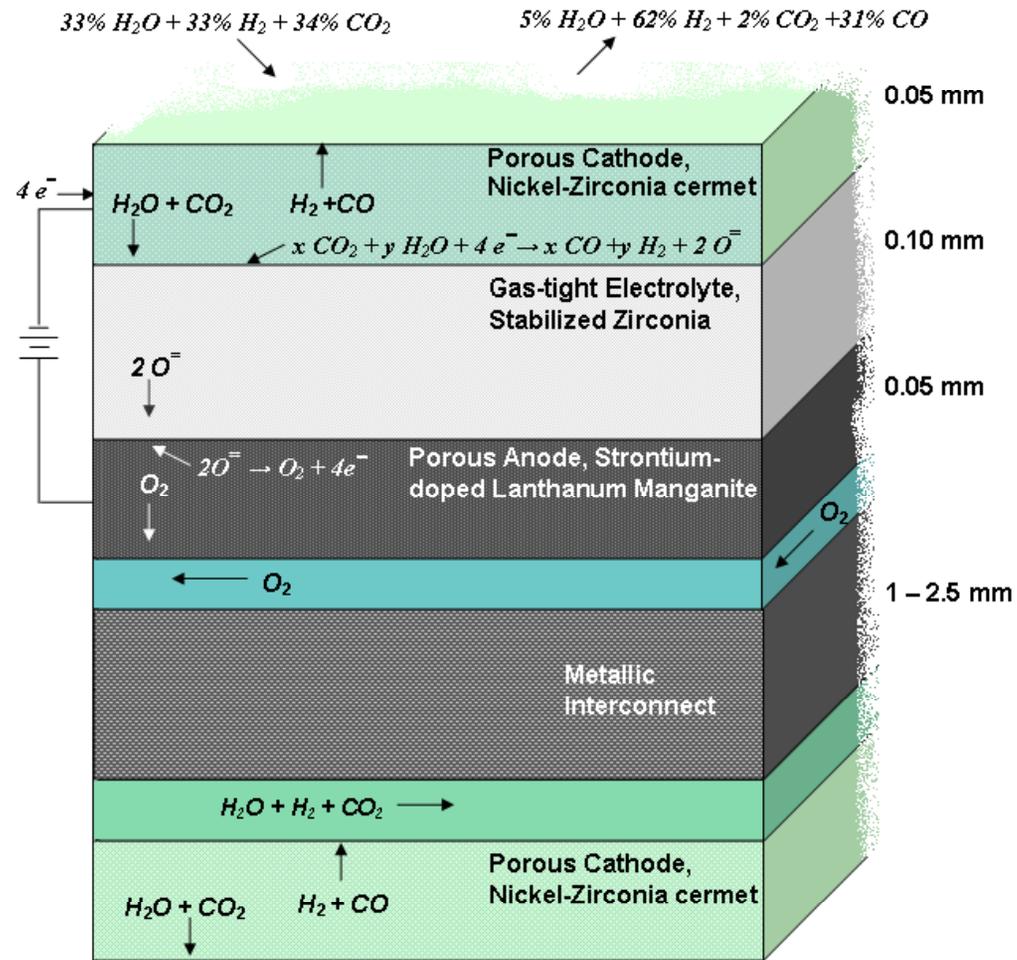
SYNTHETIC FUELS

- Nothing New About Synfuels
 - Produced via the Fischer-Tropsch process

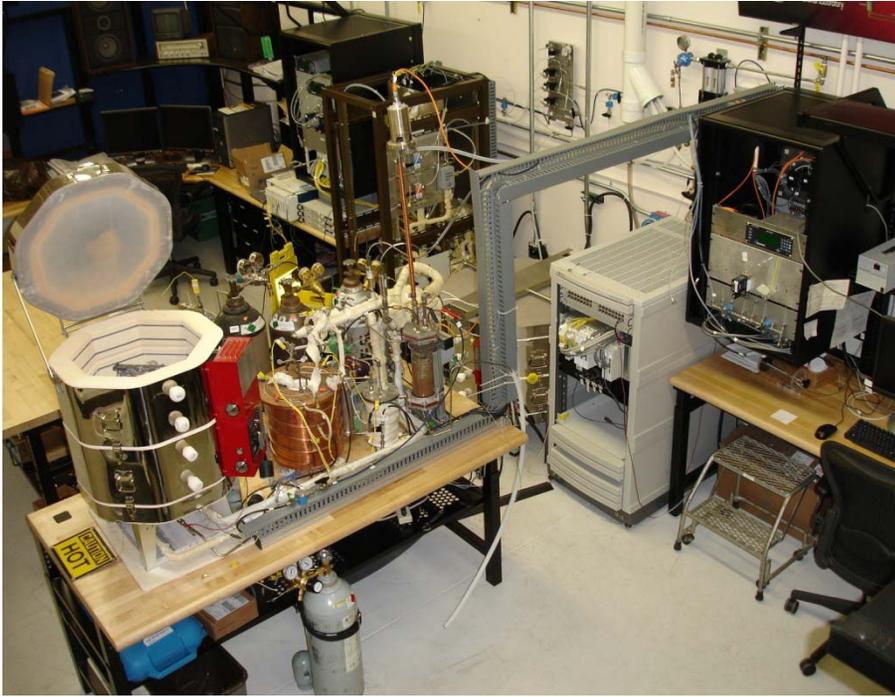
Syngas

- $n\text{CO} + (2n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$
- Discovered before WWII
- Pressure primarily determines n
- Production of Synfuels requires Syngas
 - Previous H_2 production releases large amounts of CO_2

Co-electrolysis in an solid oxide cell



INL Coelectrolysis Experiment



Products of Fischer Tropsch Synthesis



ENERGY SOURCES



Nuclear

Renewable Energies



Wind



Solar



Geothermal



Hydropower

Fossil Fuels

Coal



Natural Gas

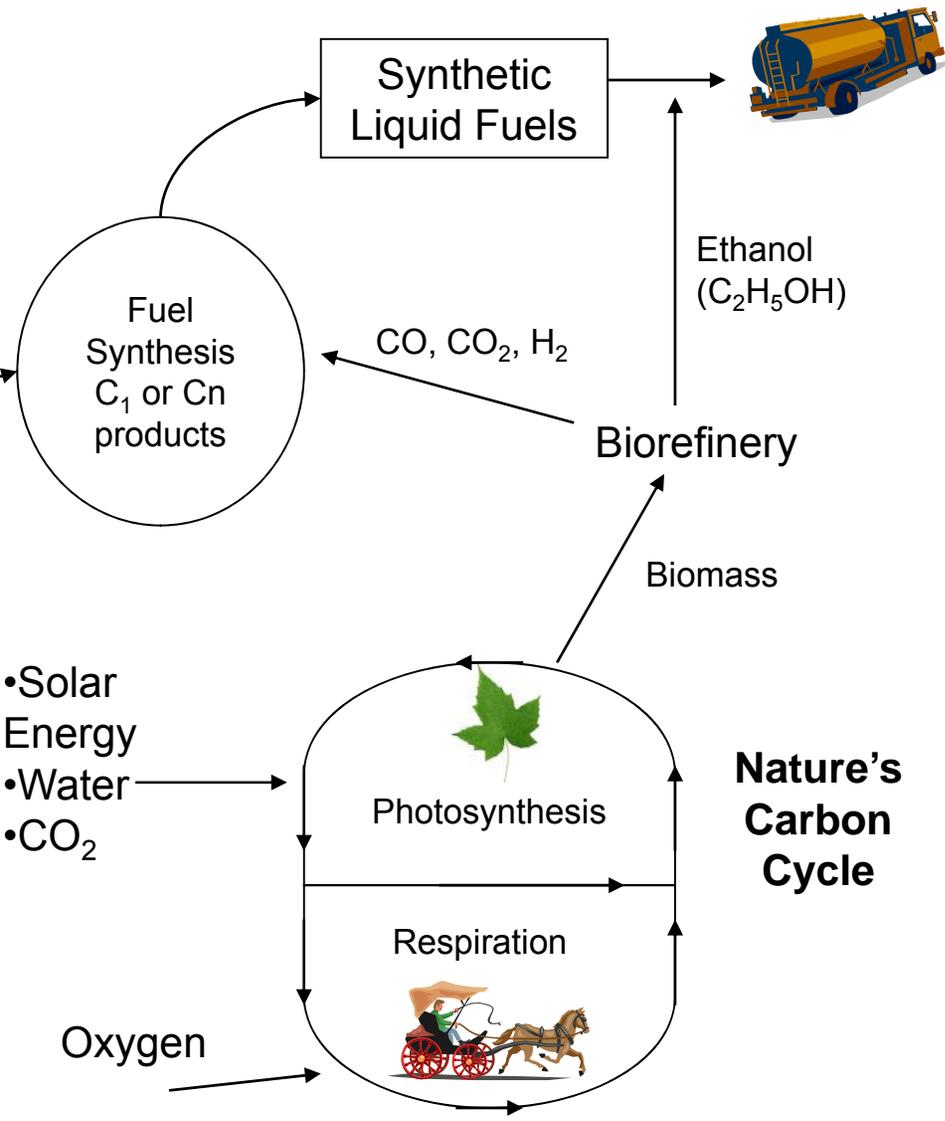


Oil



Carbon Capture

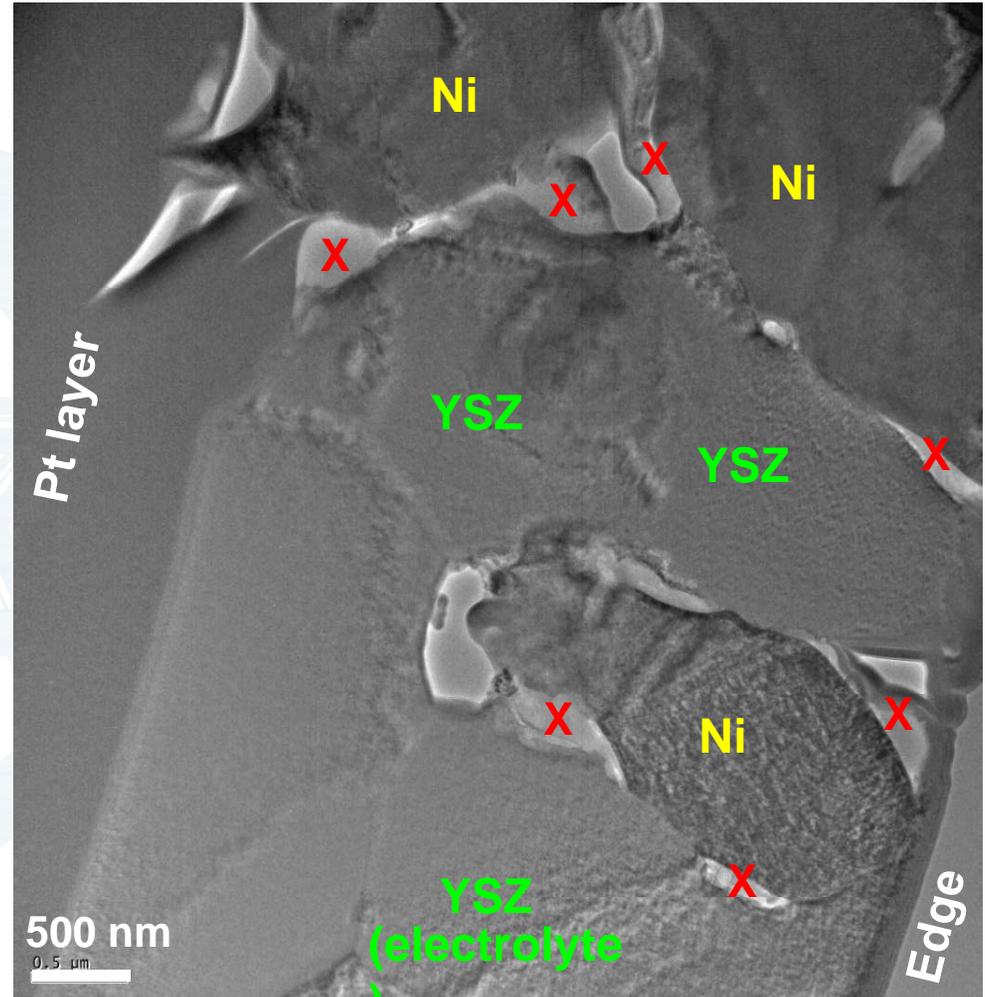
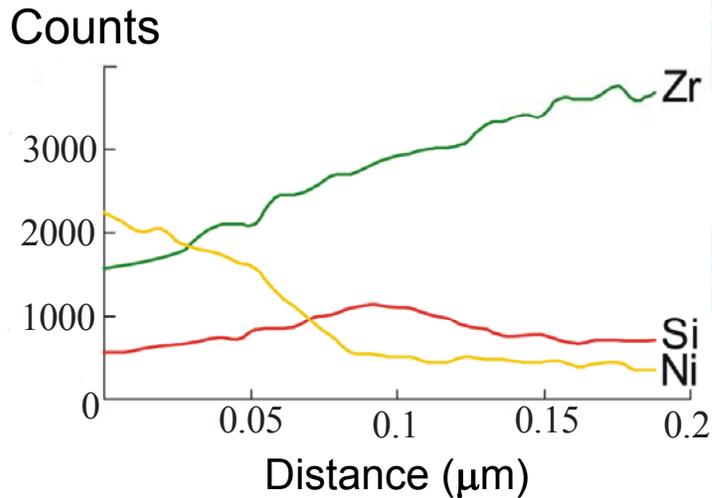
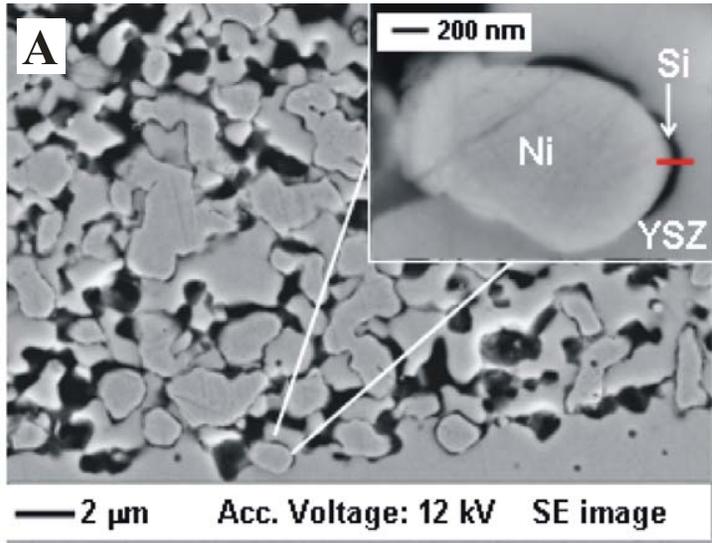
Fossil carbon sequestration



Progressive steps in the use of hydrogen produced through nuclear energy

- [now] Upgrading of current heavy crude oils for the production of gasoline
- [2015] Upgrading of the Athabasca Oilsands for the production of diesel and gasoline
- [2020] Catalytic addition of H₂ to coal (hydrogenation) to produce gasoline
- [2025] Fischer-Tropsch synthesis of diesel and jet fuel using CO from coal gasification and H₂ from nuclear energy
- [2035] Co-electrolysis of CO₂ from biomass and steam to produce CO and H₂ for synthetic, GHG-neutral, gasoline, diesel and jet fuels
- [2050] Nuclear production of H₂ for use in fuel-cell-powered vehicles.

3. Focus on Post-mortem Analysis - Impurities



- "text book" example of impurities at TPBs

A. Hauch et al., *J. Electrochem. Soc.*, **154**(9), A619-A626, 2007

Conclusions

- **Conventional electrolysis is available today**
- **High temperature electrolysis is under development and will be more efficient**
- **HTE Experimental results from 25-cell stack and 2x60-cell half-module, fabricated by Ceramatec,**
 - **Hydrogen production rates in excess of 160 normal (0° C, 1 atm) liters/hour were maintained with a 10-cell solid-oxide electrolysis stack for 2500 hours (May-Sept 2009)**
 - **The Integrated Laboratory Scale experiment at the INL operated for 1080 hours in Sept-Oct. 2008, producing a maximum of 5.65 Nm³/hr (0.504 kg/hr) of H₂.**
- **In the near-term hydrogen from nuclear energy will be used to upgrade crude and later to synthesize conventional gasoline and diesel fuel from renewable carbon sources**
- **In the long-term pure hydrogen from nuclear energy may power vehicles directly through fuel cells**

**But will there be
enough uranium or thorium?**

Nuclear Fuel – the basic facts

- **Natural uranium: 99.3% ^{238}U and 0.7% ^{235}U**
- **^{235}U is the only naturally-occurring fissile isotope**
- **Thorium (100% ^{232}Th) is about 3.9 time more abundant than Uranium, but ^{232}Th is not fissile**
- **^{232}Th can be bred to fissile ^{233}U and ^{238}U to ^{239}Pu**

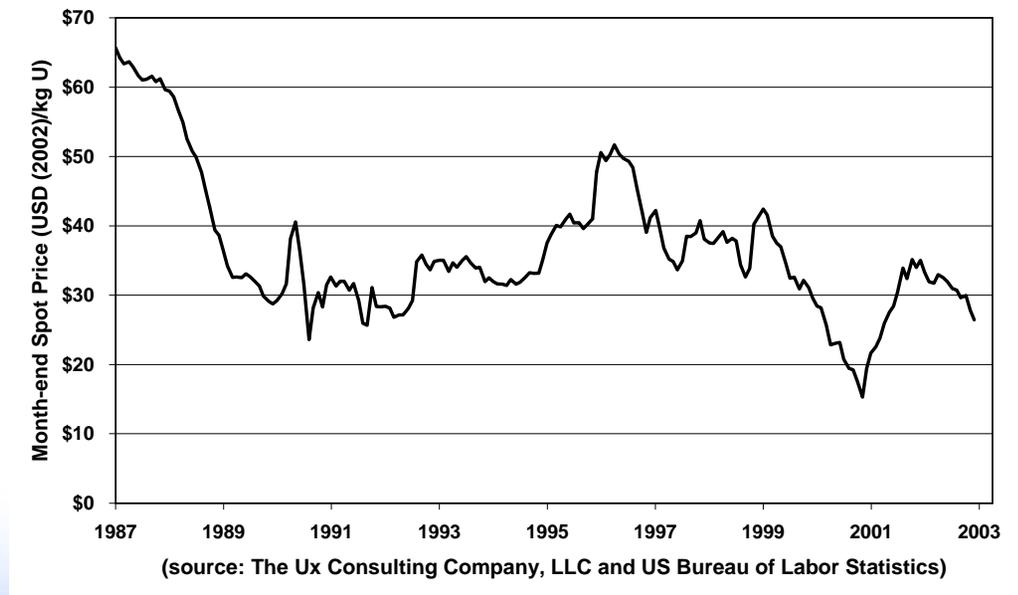
- **World consumption of natural uranium is about 60,000 tons per year.**
 - **75% of the energy is due to the fission of ^{235}U**
 - **25% is due to ^{239}Pu fission**

Past considerations of Uranium Resources

- Based on field exploration and information of proven resources by mining companies
- **Red Book** – compiled annually by the Nuclear Energy Agency of the Organization for Economic Cooperation and Development (NEA-OECD)
 - ~4 million tons ‘proven’ reserves
(implying that we only have ~70 years’ reserves at present consumption rates)
 - ~10 million tons ‘speculative’ reserves

Because of low prices, little exploration has occurred in the last 25 years.

- Slow growth in nuclear power worldwide
- Development of higher burn-up fuels
- Downblending of highly enriched uranium to reactor grade (<5% ^{235}U)

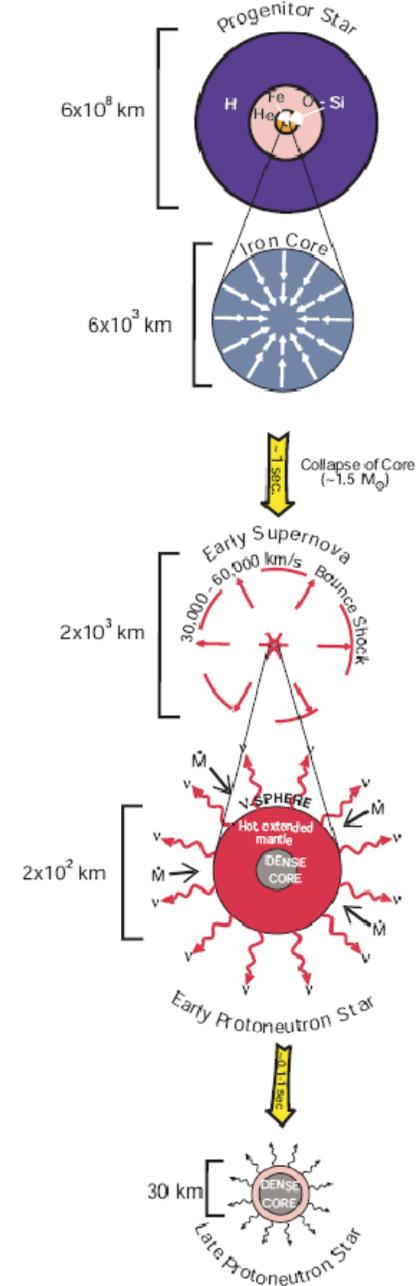


A more Fundamental Look at Uranium Resources

- How is uranium created?**
- How much uranium is created compared to other elements?**
- How are these various elements formed into planets?**
- How is uranium transported within the earth?**
- Can we measure the uranium inventory of the earth?**

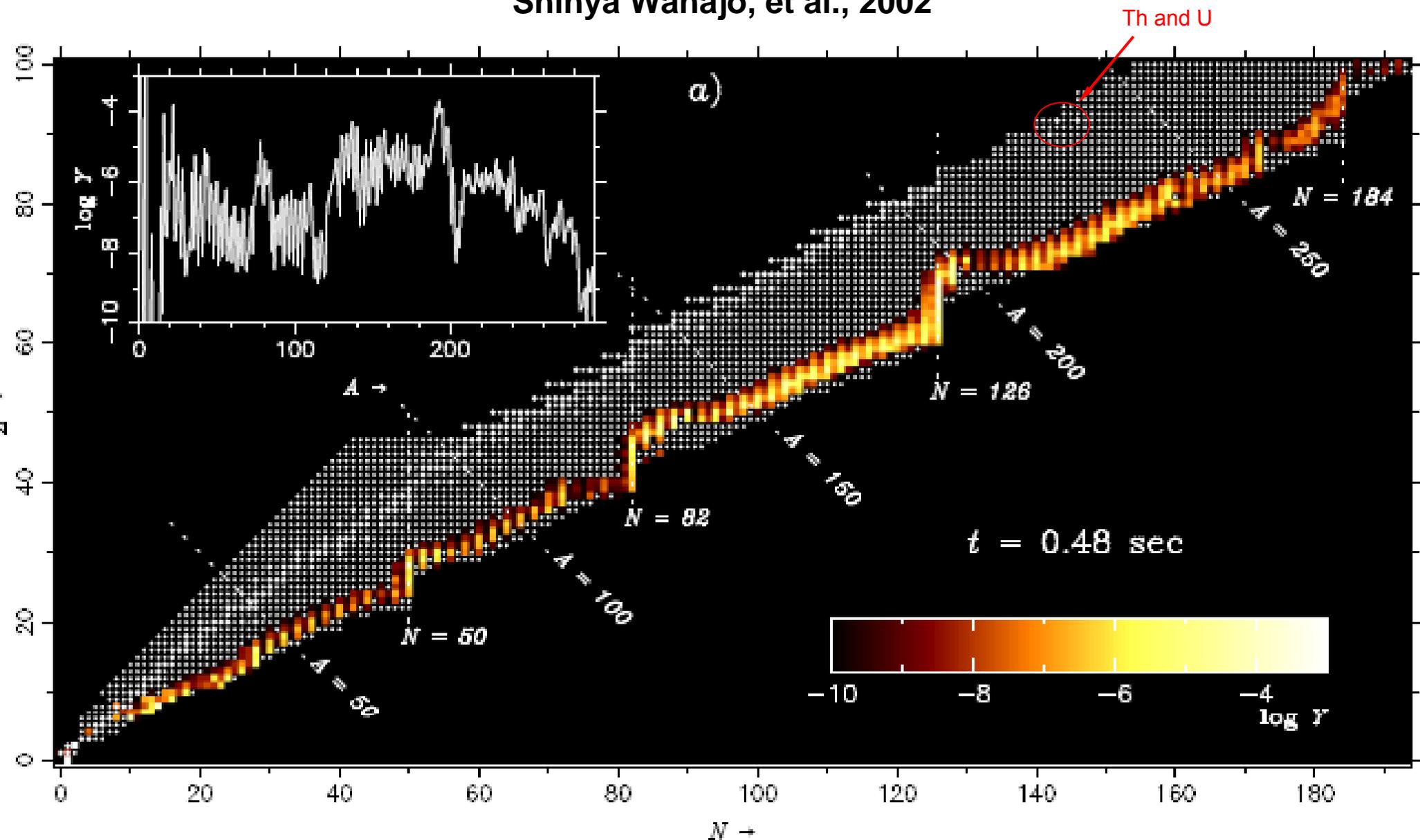
The origin of Uranium

- A star the mass of the Sun lasts for 10 billion years but can only produce elements up to iron
- A star 10 times the mass of the Sun lasts 10 million years until it explodes as a supernova, producing all the elements in the periodic table.
- About one supernova per second in the universe

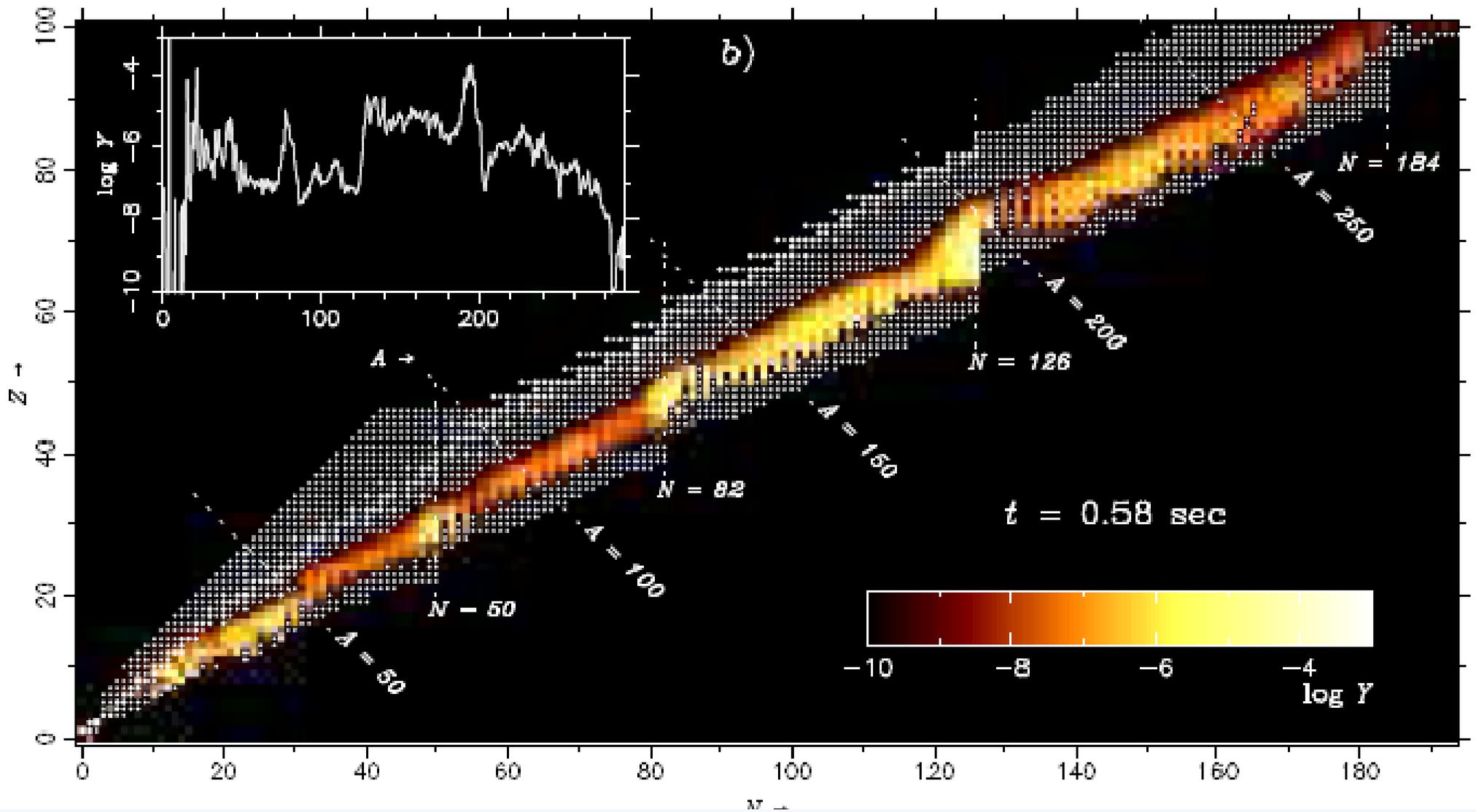


Two seconds in a supernova

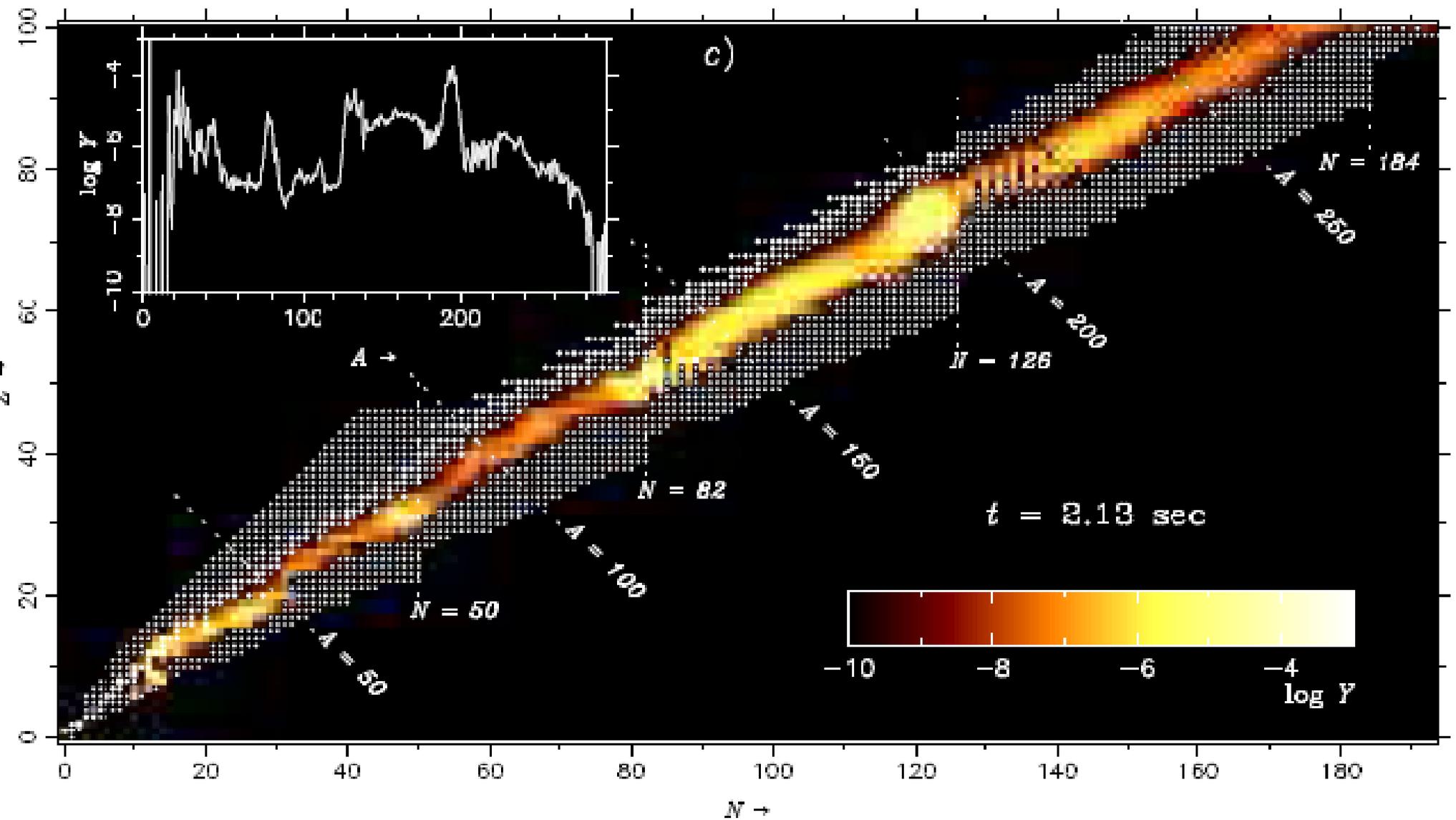
Shinya Wanajo, et al., 2002



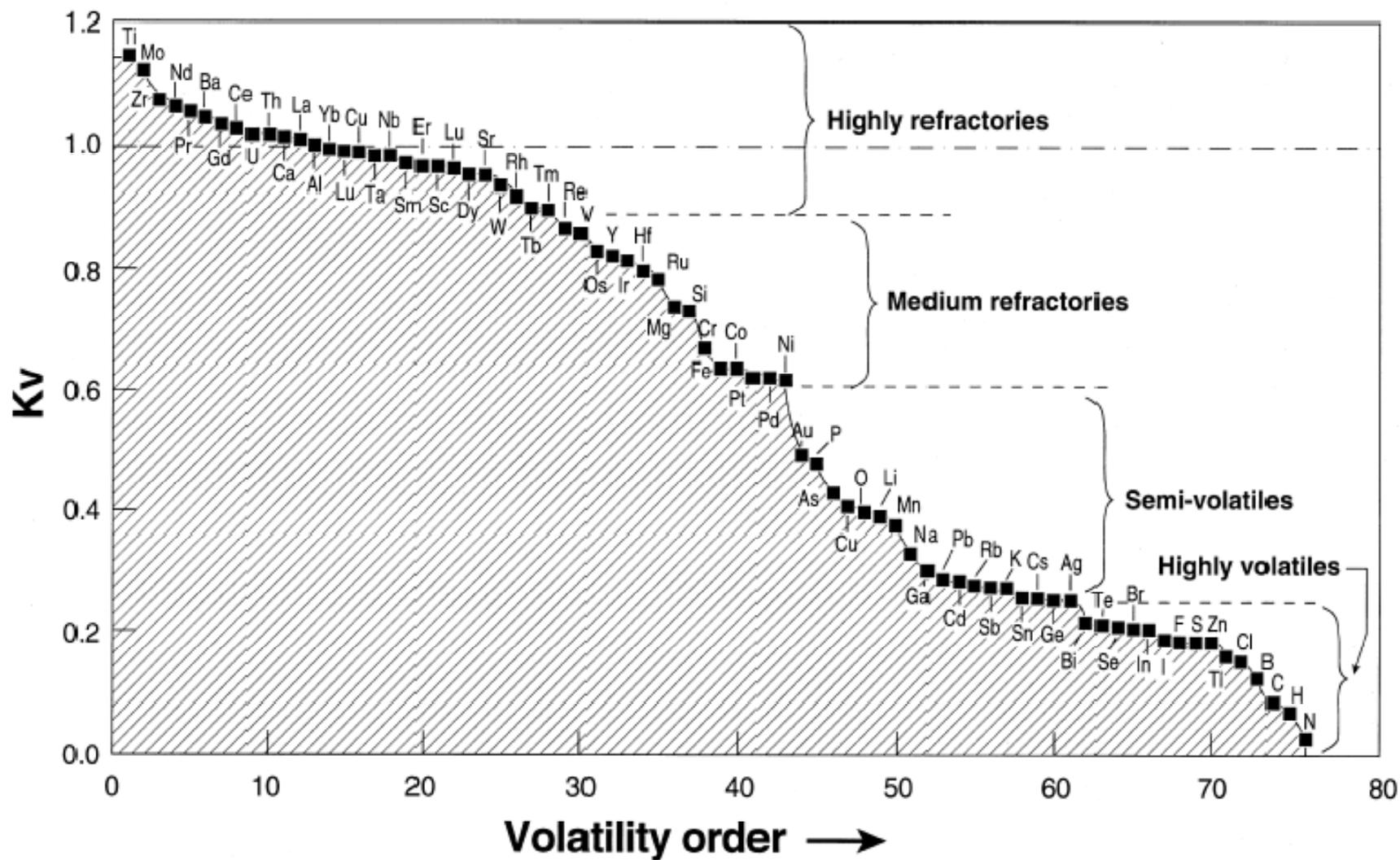
Two seconds in a supernova



Two seconds in a supernova



Relative Volatilities



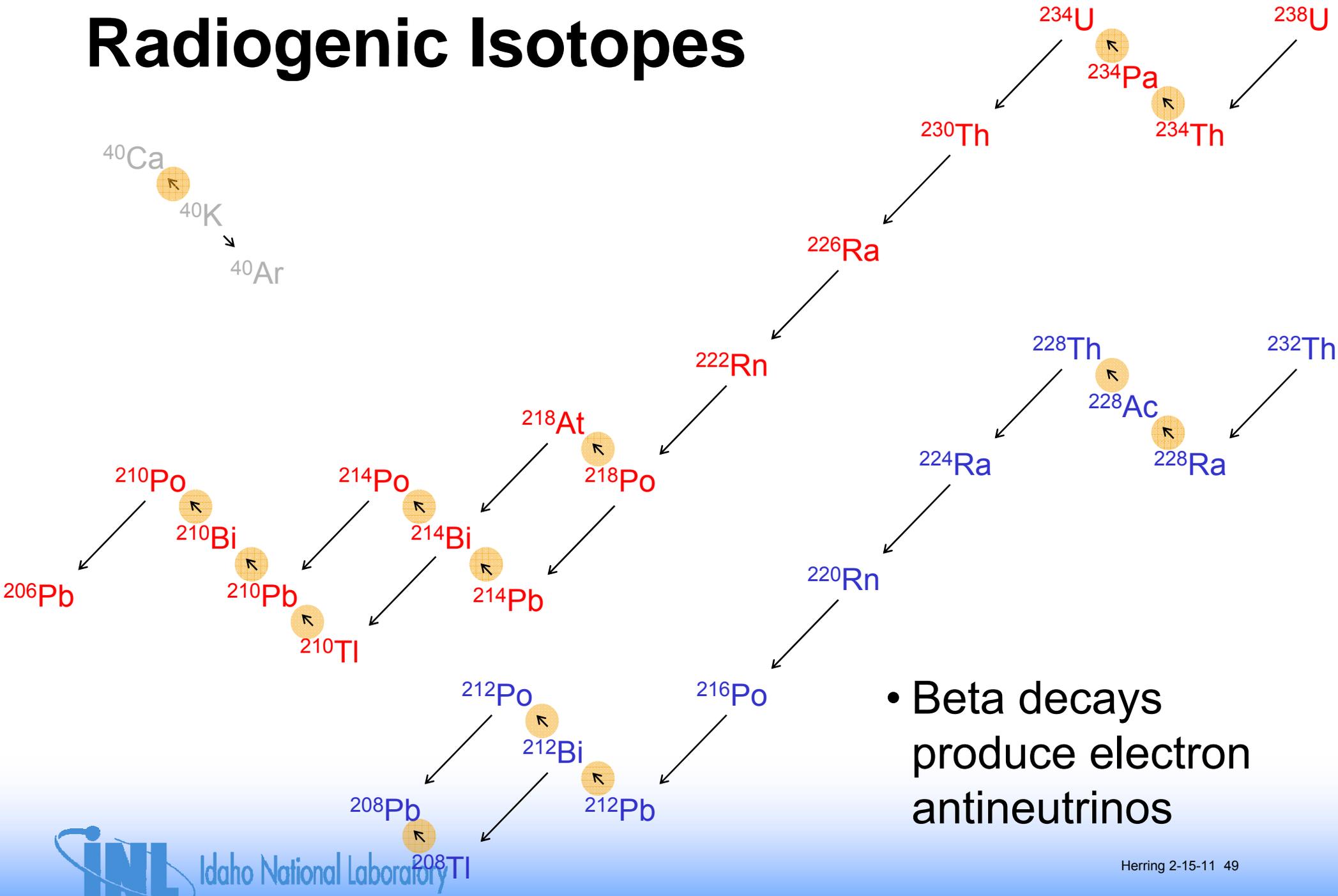
Conclusions from Uranium Nucleosynthesis

- Uranium should be $\sim 10^{-7}$ to 10^{-6} the mass of silicon in the debris of a supernova
- With a half-life of 4.5 billion years, ^{238}U has decayed about a factor of 5 since the average supernova
- Silicon has similar oxide-forming and planetary accretion characteristics to uranium
- The earth is $\sim 10\%$ Si, so it should be ~ 10 ppb U

Geoneutrinos as evidence of the Global Uranium Inventory

- Neutrinos are elementary particles
- travel close to, but not at, the speed of light
- lack an electric charge
- able to pass through ordinary matter almost undisturbed
 - thus extremely difficult to detect
- have a minuscule, but non-zero, mass
- usually denoted by the Greek letter ν (nu).
- created as a result of certain types of radioactive decay or nuclear reactions
- three types: electron, tau, and muon
- both neutrinos and anti-neutrinos

Radiogenic Isotopes



- Beta decays produce electron antineutrinos

Sources of Geoneutrinos

Table 1

The main properties of geo-neutrinos.

| Decay | Q [MeV] | $\tau_{1/2}$ [10^9 yr] | E_{\max} [MeV] | ϵ_H [W/Kg] | $\epsilon_{\bar{\nu}}$ [$\text{kg}^{-1}\text{s}^{-1}$] |
|--|--------------|------------------------------|---------------------|------------------------|---|
| $^{238}\text{U} \rightarrow ^{206}\text{Pb} + 8\ ^4\text{He} + 6e + 6\bar{\nu}$ | 51.7 | 4.47 | 3.26 | 0.95×10^{-4} | 7.41×10^7 |
| $^{232}\text{Th} \rightarrow ^{208}\text{Pb} + 6\ ^4\text{He} + 4e + 4\bar{\nu}$ | 42.7 | 14.0 | 2.25 | 0.27×10^{-4} | 1.63×10^7 |
| $^{40}\text{K} \rightarrow ^{40}\text{Ca} + e + \bar{\nu}$ | 1.32 | 1.28 | 1.31 | 0.36×10^{-8} | 2.69×10^4 |

Table 2

U, Th and K according to BSE

| | m [10^{17} kg] | H_R [10^{12} W] | L_{ν} [10^{24} s^{-1}] |
|-----------------|------------------------|-------------------------|--|
| U | 0.8 | 7.6 | 5.9 |
| Th | 3.1 | 8.5 | 5.0 |
| ^{40}K | 0.8 | 3.3 | 21.6 |

Fiorentini, et al. 14 Sep 2004

Characteristics of Geoneutrinos

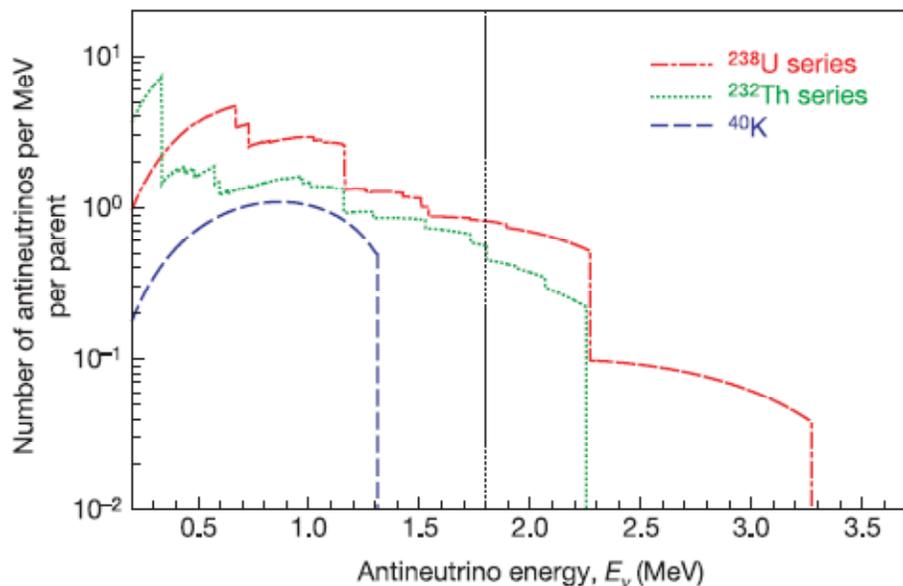


Figure 1 | The expected ^{238}U , ^{232}Th and ^{40}K decay chain electron antineutrino energy distributions. KamLAND can only detect electron antineutrinos to the right of the vertical dotted black line; hence it is insensitive to ^{40}K electron antineutrinos.

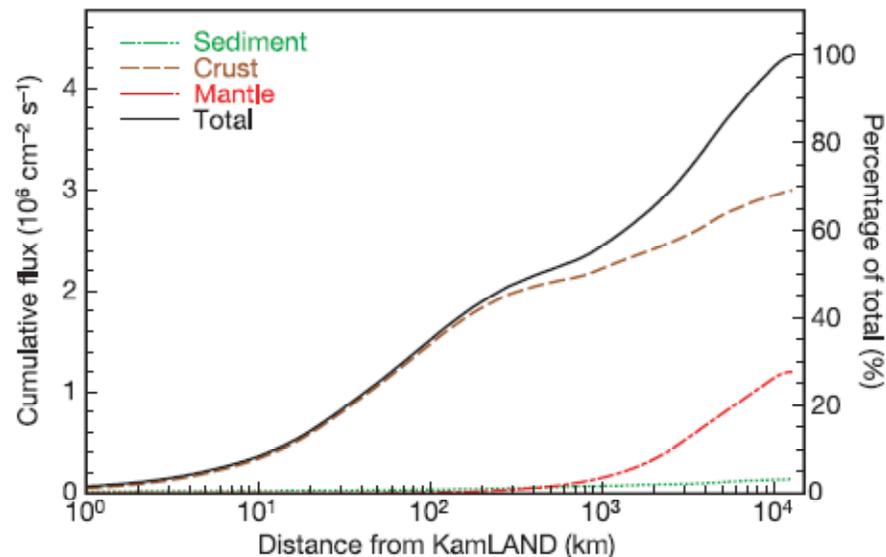
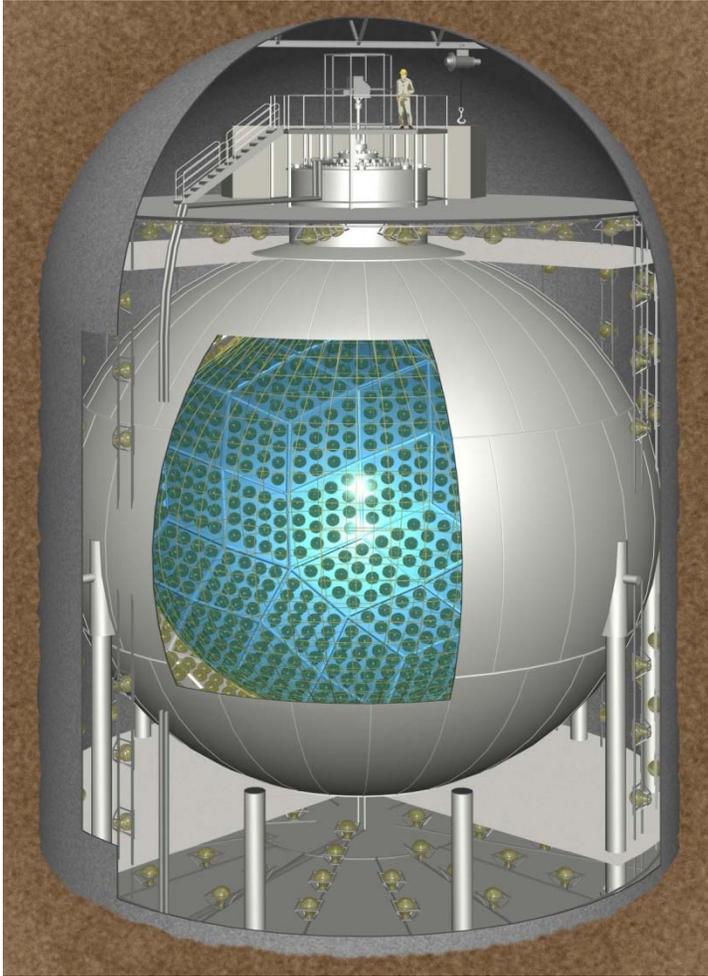


Figure 2 | The expected total ^{238}U and ^{232}Th geoneutrino flux within a given distance from KamLAND²². Approximately 25% and 50% of the total flux originates within 50 km and 500 km of KamLAND, respectively. The line representing the crust includes both the continental and the almost negligible oceanic contribution.

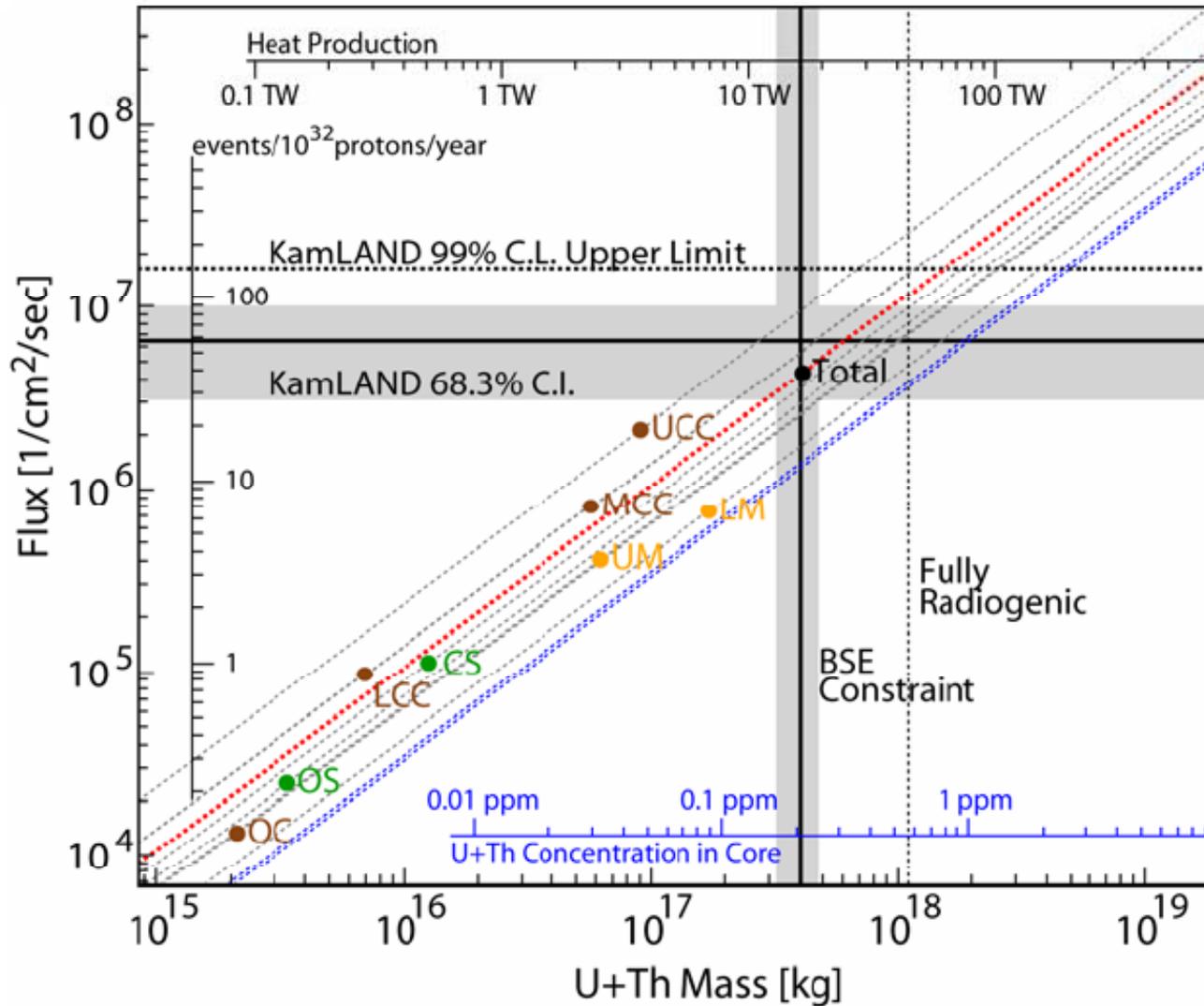
Araki, et al., Nature, 7-28-05

KamLAND style detector



- **1kton liquid scintillator.**
- **~20m diameter sphere.**
- **Monolithic:**
 - **Lower radioactive backgrounds**
 - **Fully contained events**

KamLAND Geoneutrino Data



$U+Th = 3E17 \text{ kg} \rightarrow U = 6E16 \text{ kg} = 10 \text{ ppb of } m_{\text{earth}}$

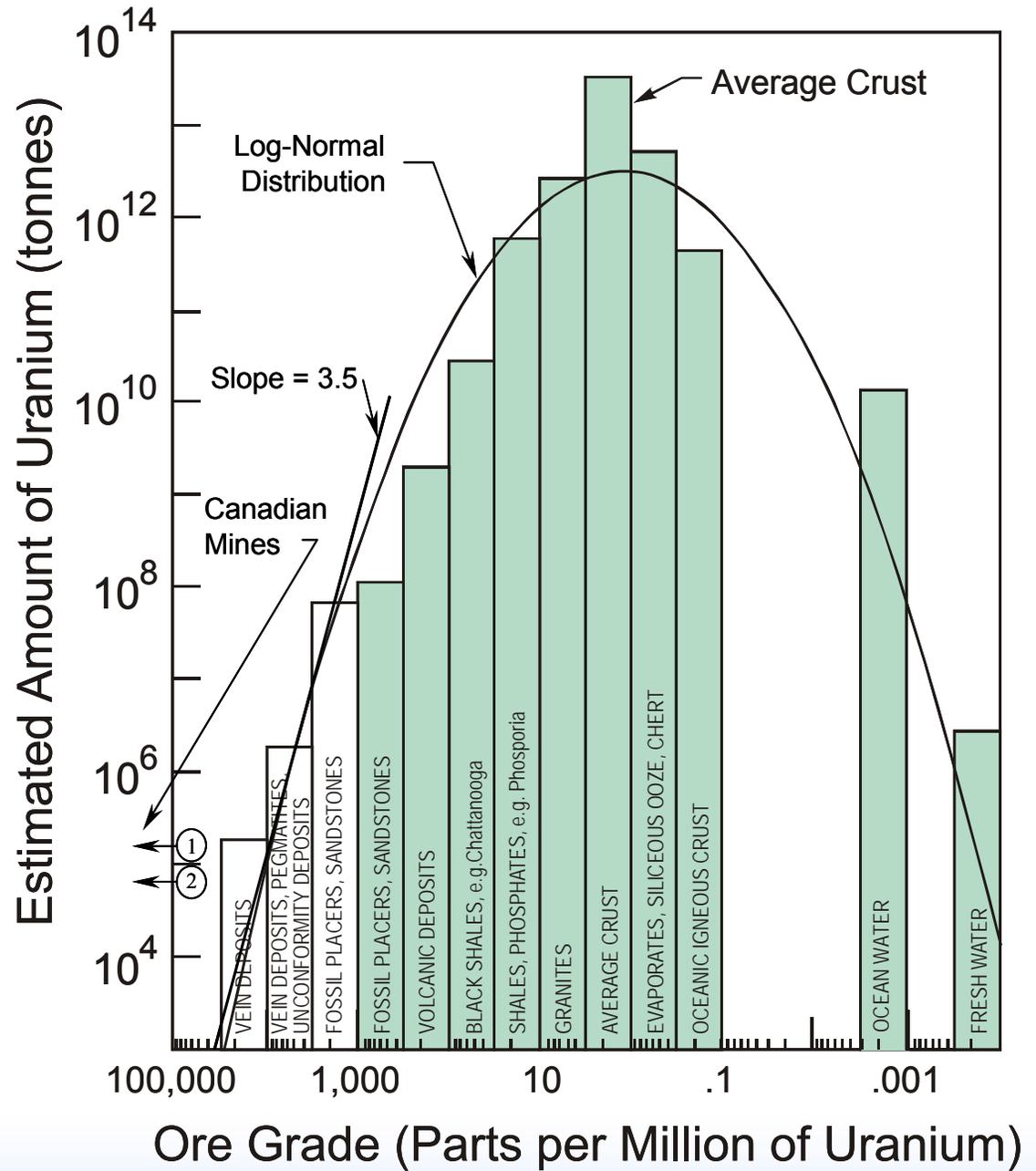
Enomoto, et al., 2005



Conclusions from the Geoneutrino Data

- **The geoneutrino data roughly agrees with the astrophysical models for uranium nucleosynthesis (and asteroid analyses)**
- **Most of the uranium is in the continental crust**
- **The global inventory of uranium exceeds the Red Book estimates by several orders of magnitude**

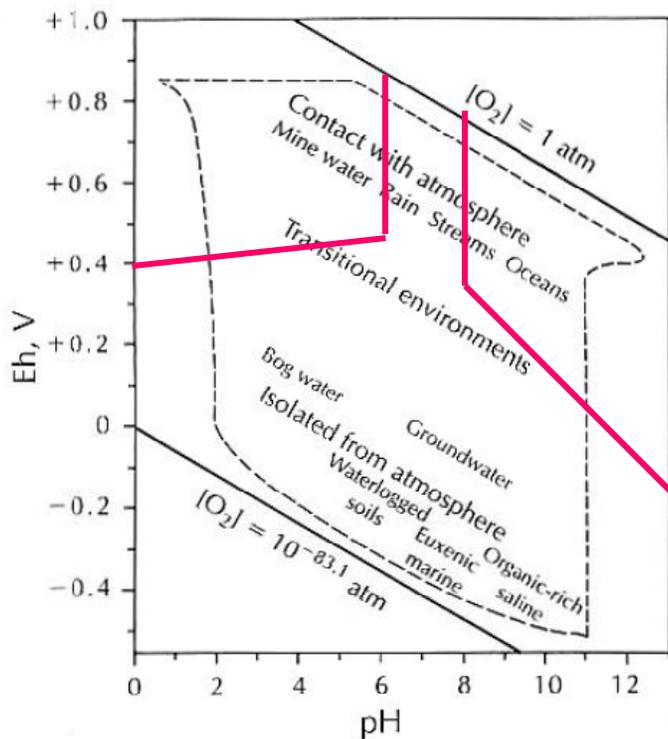
Uranium-containing Minerals



(1) the McArthur River deposit, 137,000 t U of proven reserves averaging 18 wt% U and (2) the Cigar Lake deposit, 90,000 t U at an average grade of 17 wt % U

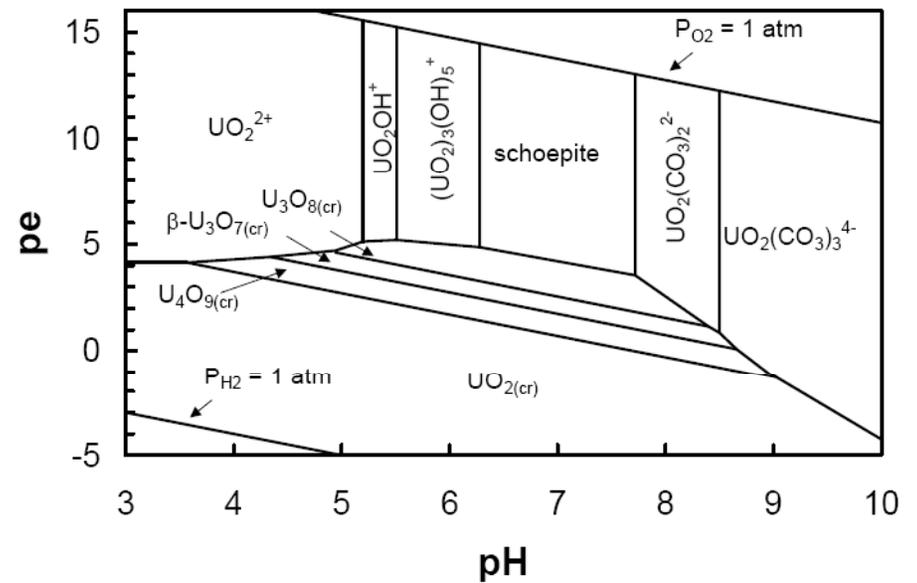
(after Deffeyes 1978, 1980)

Transport of Uranium in Water-Oxygen Environments



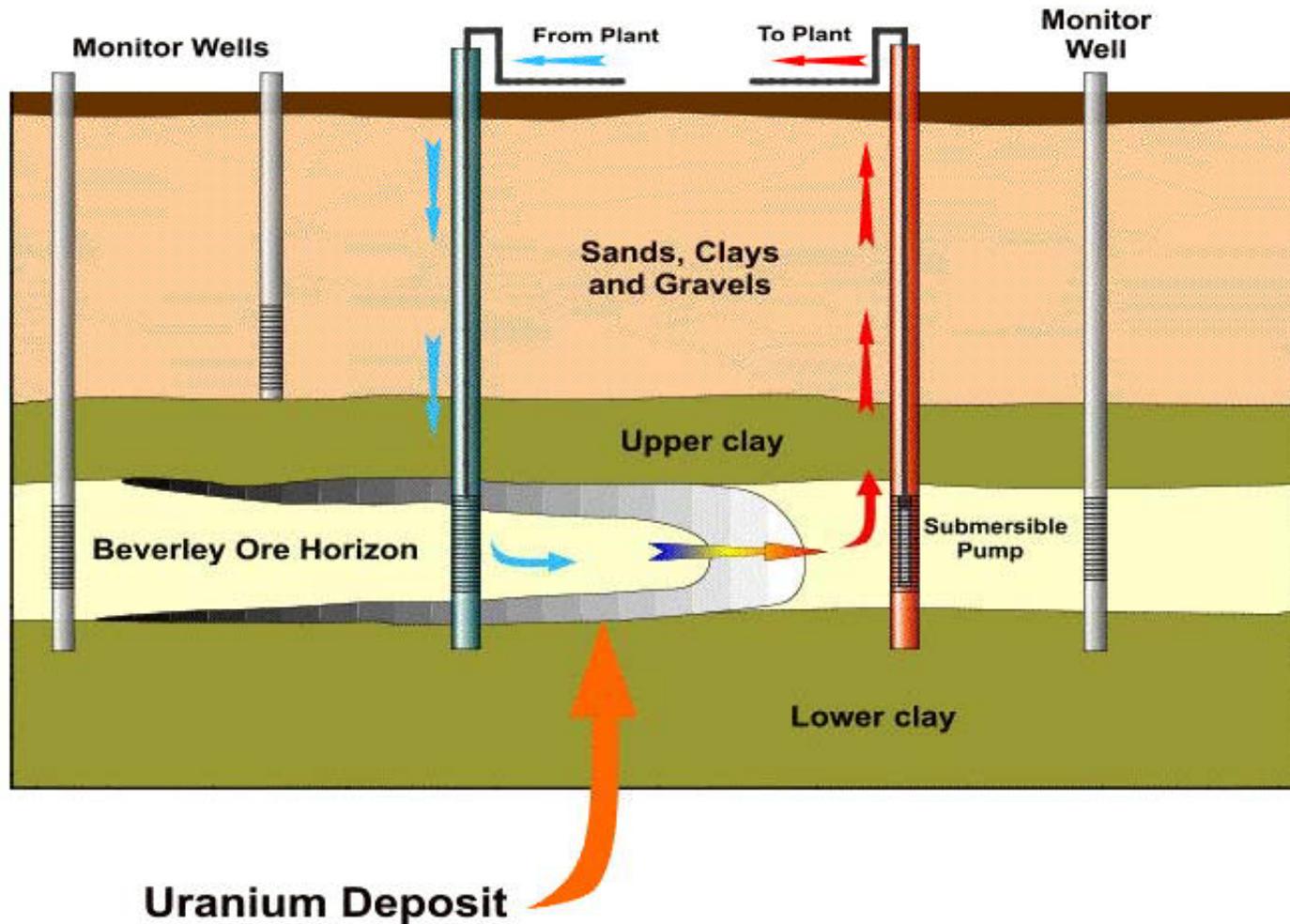
Kehew 2001

Range of Eh-pH conditions in natural environments based on data of Baas-Becking et al. (1960) Jour. Geol. 68: 243-284.



Giammar Caltech thesis 2001

In situ Leaching of uranium



Recent Indications of Larger Uranium Resources

BHP Billiton boosts uranium resource at Olympic Dam

27 September 2007

In the course of identifying a 77% increase in mineral resources, BHP Billiton has defined a 27% increase in uranium resources, to 2.24 million tonnes of uranium oxide (1.9 million tU), at the Olympic Dam mine in South Australia. Known copper has increased 38% to 67 million tonnes and gold to 2450 tonnes.

The new figures are based on 2095 km of drilling over the last two years, both from surface and underground, and confirm the deposit as the world's largest for uranium. It covers an area of over 6 km by 3.5 km, is up to 2 km deep and remains open laterally and at depth as the drilling program continues.

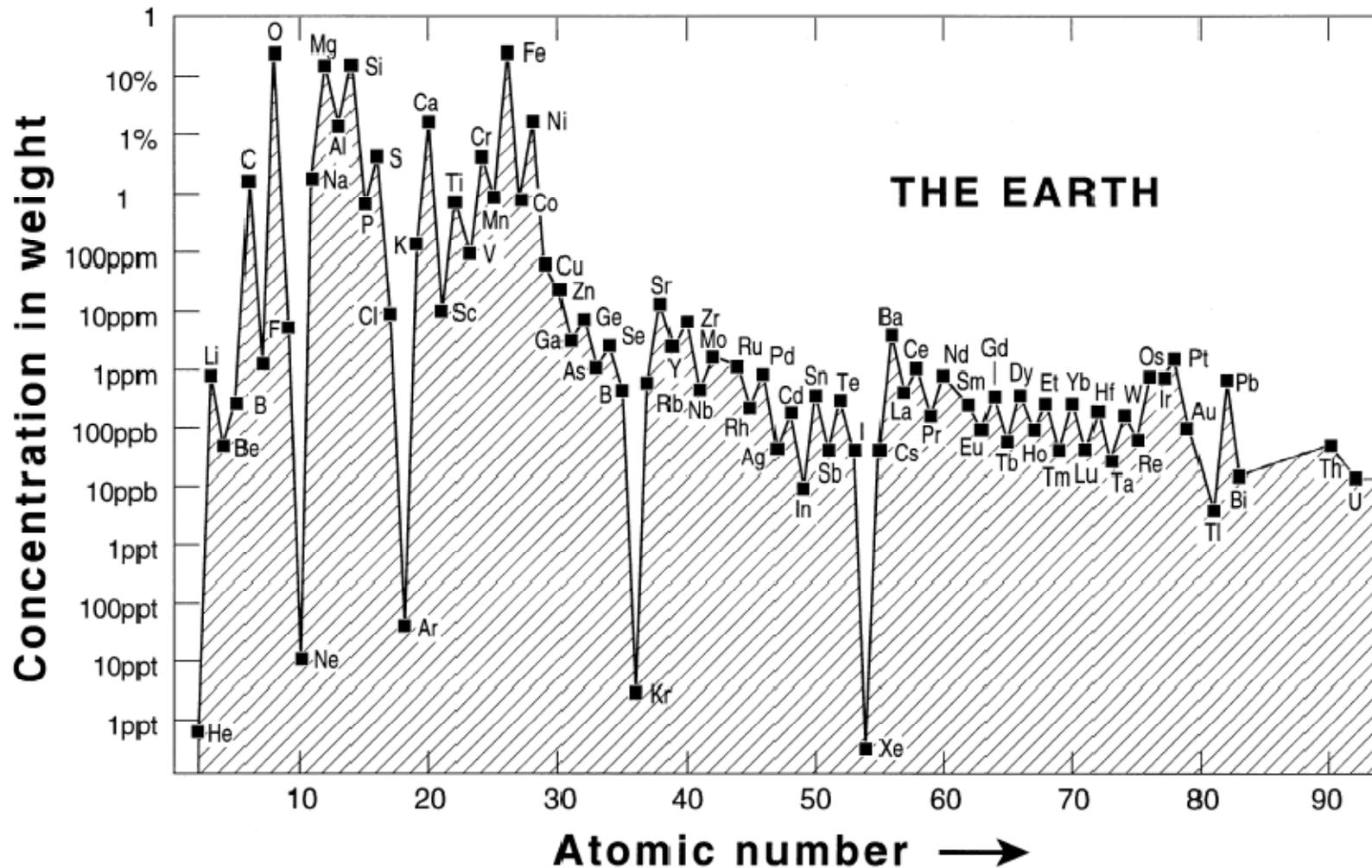
A preliminary feasibility study on tripling production is due for completion in 2008. If implemented, this would increase production to about 15,000 tonnes per year of uranium oxide (12,700 tU). Production in 2006-07 was 3474 tonnes U₃O₈ (2946 tU).



The processing plant at Olympic Dam (Image: BHP Billiton)

WNN 9-27-07

The Bulk Silicate Earth (BSE)



Conclusions

- **Nuclear-produced H₂ can make a crucial contribution to future transportation fuels**
- **The first uses of that hydrogen will be to upgrade unconventional fossil fuels**
- **Data from several independent methods suggest that there is far more uranium than conventionally estimated**
- **Most of that uranium is in the upper continental crust**
- **The challenge will be in extracting that U + Th with minimal environmental impact, e.g. occupation hazards, tailings piles and radon release**
 - **In situ leaching**
 - **Co-production of uranium with other minerals**
- **The overall challenge in the nuclear fuel cycle is the management of actinides and long-lived fission products**