Status of Skutterudite-Based Segmented Thermoelectric Technology Components Development at JPL

23rd Symposium on Space Nuclear Power and Propulsion
STAIF 2006

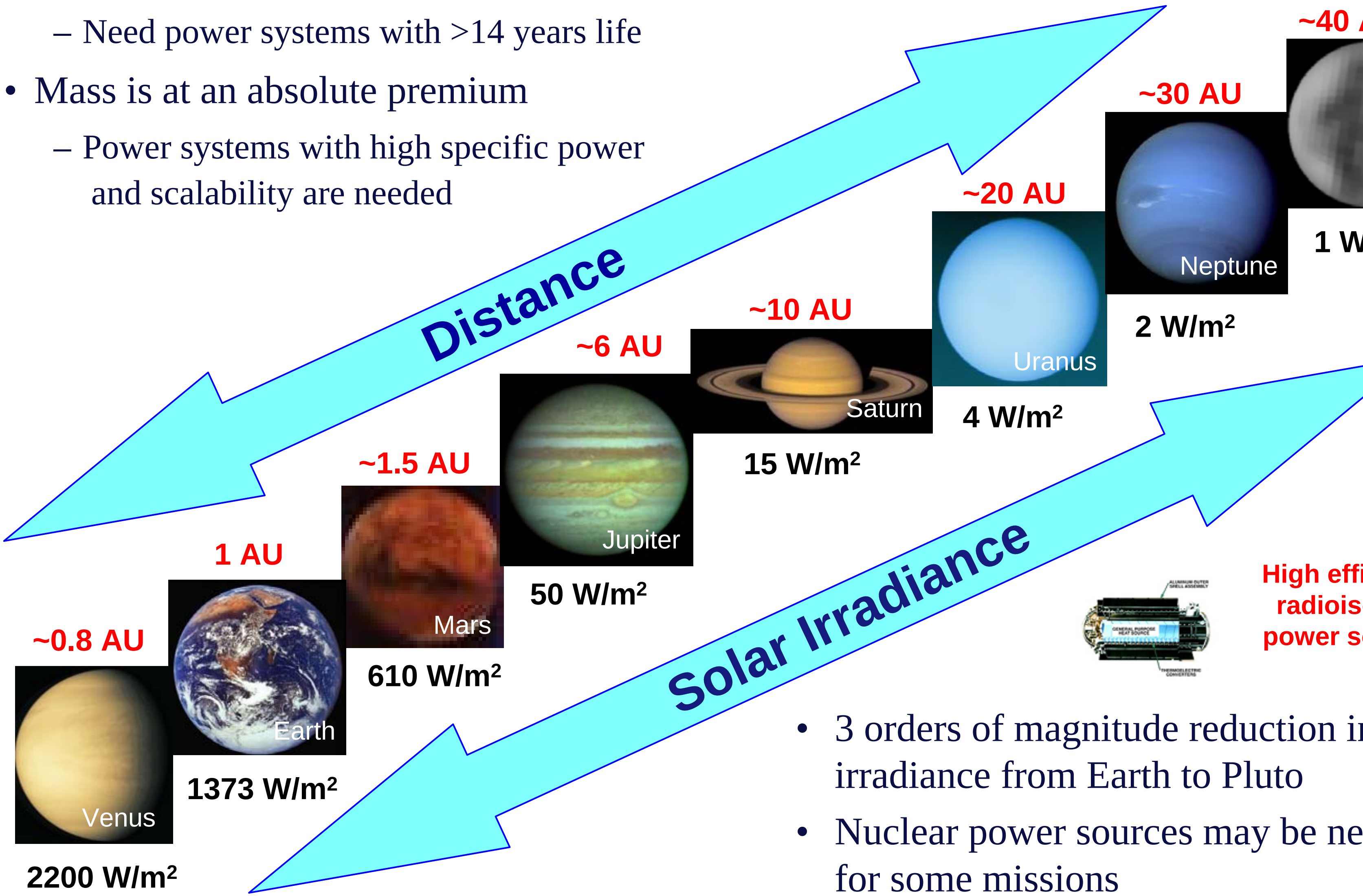
T. Caillat, J. Sakamoto, A. Jewell, C. - K. Huang, J. Cheng, J. Paik, P. Gogna, J. P-. Fleurial and R. Ewell

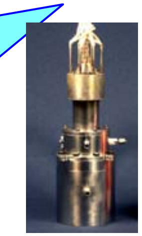
Jet Propulsion Laboratory/California Institute of Technology

Acknowledgements:
NASA

Space Power Technology

- Missions are long
  - Need power systems with >14 years life
- Mass is at an absolute premium
  - Power systems with high specific power and scalability are needed

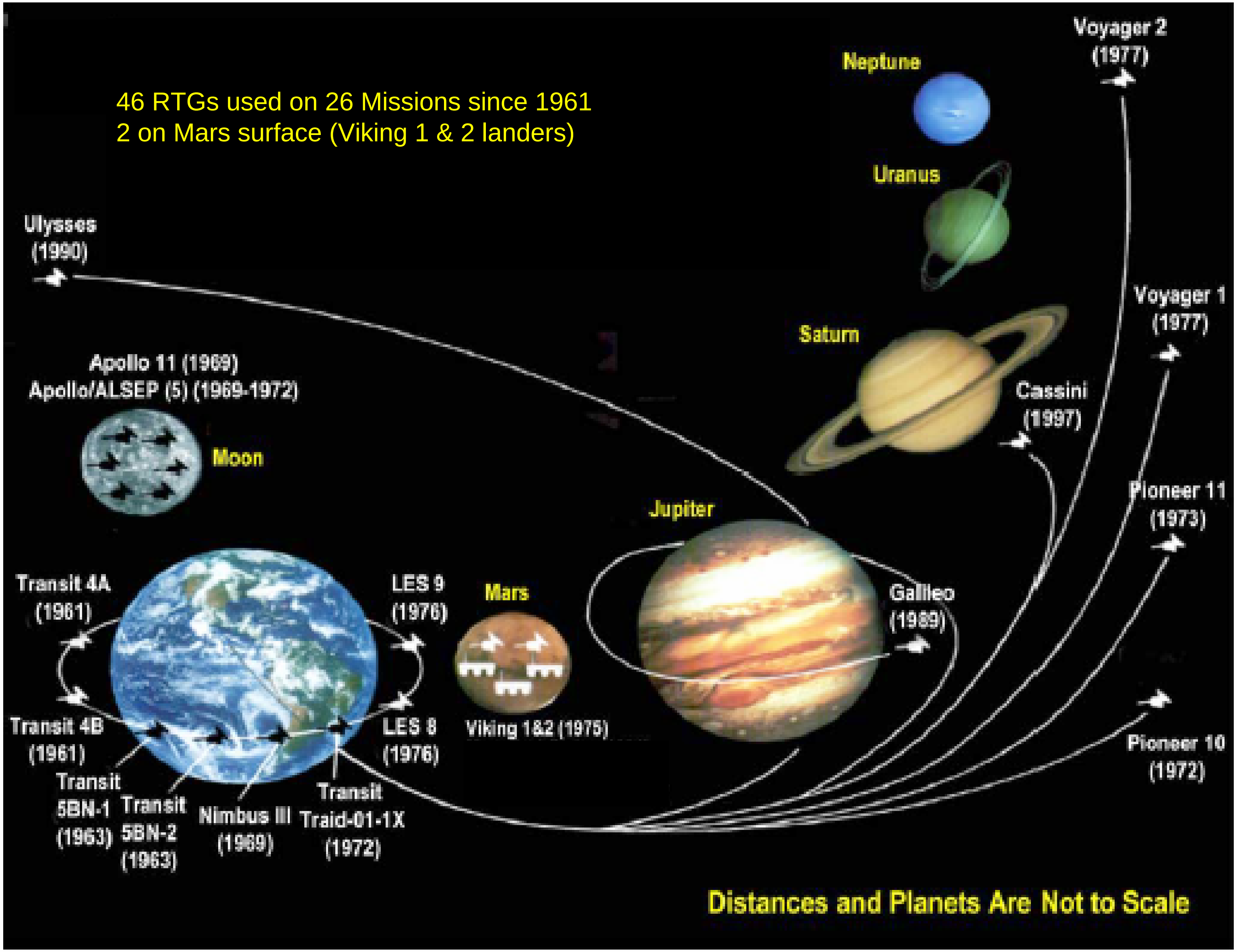




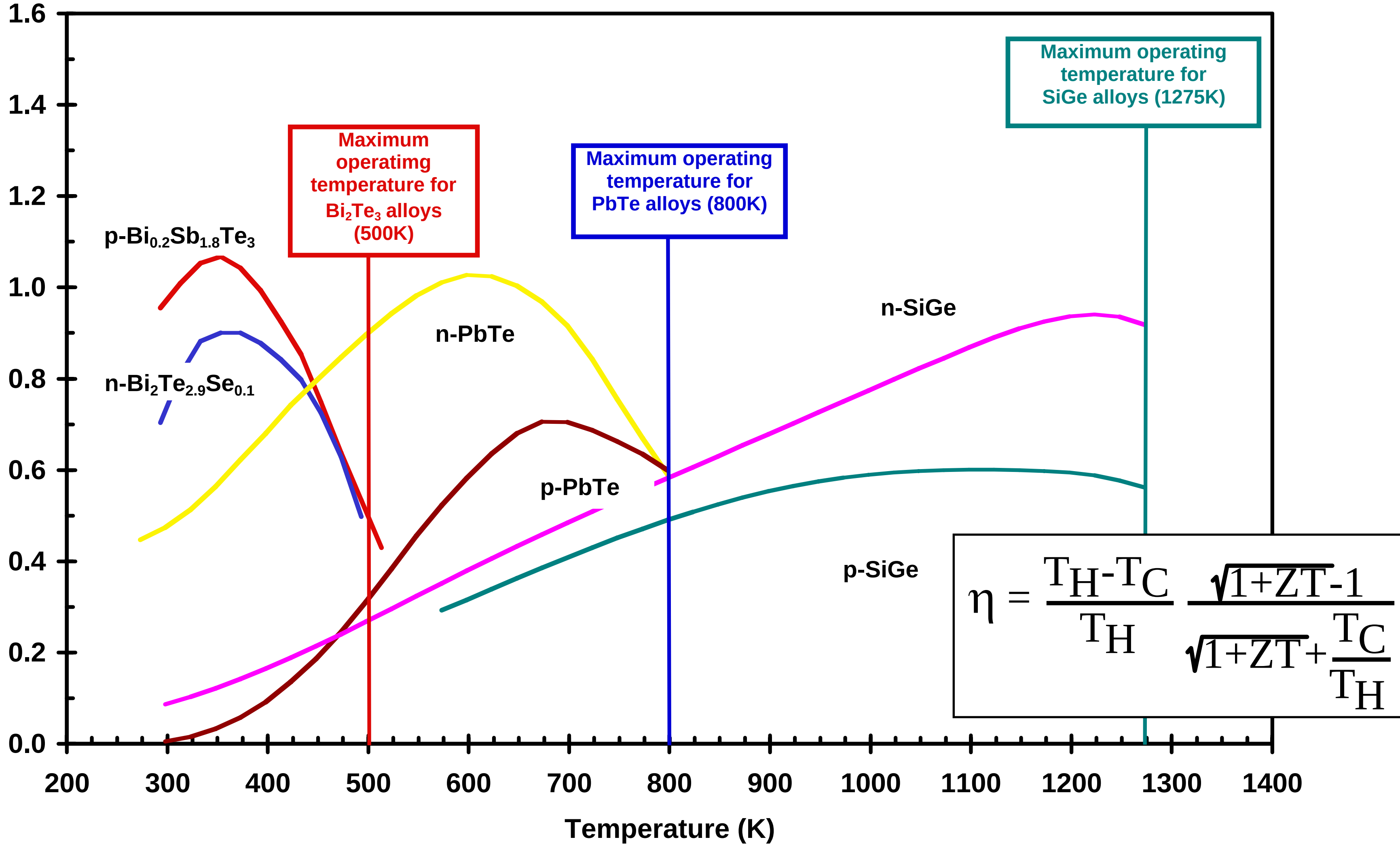
High efficiency radioisotope power sources

- 3 orders of magnitude reduction in solar irradiance from Earth to Pluto
- Nuclear power sources may be needed for some missions

U.S. space missions that have used Radioisotope Power Systems



State-of-practice thermoelectric materials



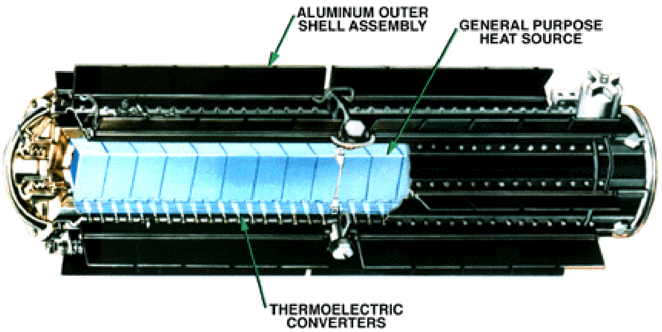
$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}}$$

Past US Radioisotope Power Systems have used either PbTe or SiGe alloys thermoelectric materials

General Purpose Heat Source RTG

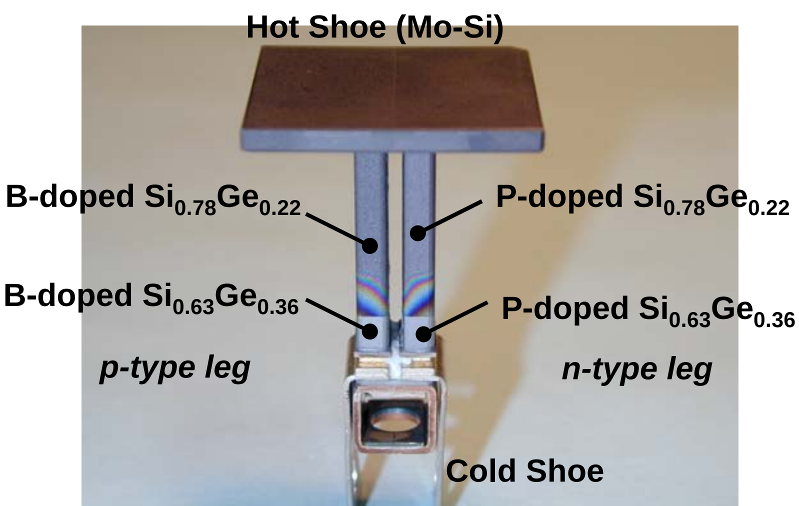
General Purpose Heat Source (GPHS)

Radioisotope Thermoelectric Generator (RTG)

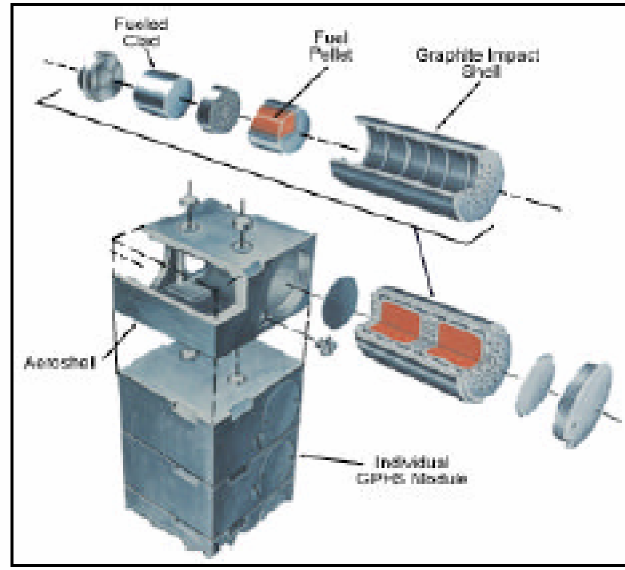


- POWER OUTPUT – 285 W(e)
- FUEL LOADING – 4400 W(t); 132,500 Ci
- WEIGHT – 124 lbs
- SIZE – 16.6 in x 44.5 in

The three Cassini Radioisotope Thermoelectric Generators (RTGs) were provided by DOE



GPHS SiGe unicouple

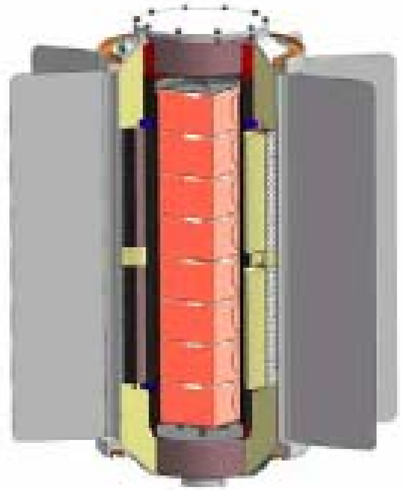


General Purpose Heat Source
(250 Watts thermal at BOL)

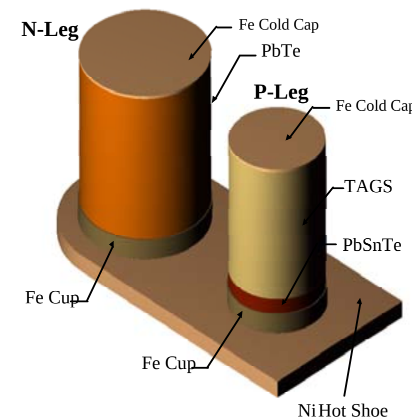
HS-RTG Performance Data

Power output-We	290 beginning of life 250 end of life
Operational life - hrs	40,000 after launch
Weight-kg	55.5
Output voltage	28
Dimensions	42.2 diameter 114 long
Hot junction temperature-K	1270
Cold junction temperature-K	566
Fuel	PuO_2
Thermoelectric material	SiGe
Numbers of unicouples	572
Mass of Pu-238-g	7,561
Specific power - We/kg	5.1

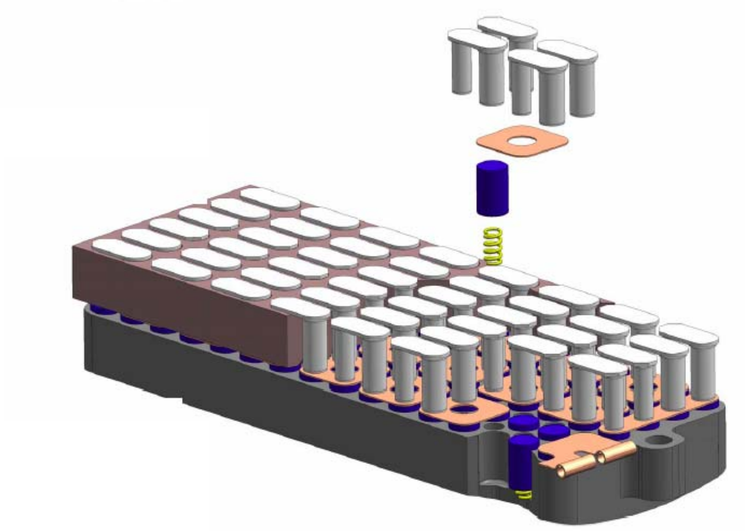
Multi-Mission PbTe/TAGS conductively coupled RTG (MMRTG)



MMRTG designed to operate both in space vacuum and planetary atmosphere



MMRTG couple



Spring-loaded TE converter

Item/Converter	PbTe/TAGS MMRTG
Hot side temperature (K)	**823**
Cold side temperature (K)	**483**
Converter efficiency (%)	**7.6**
System efficiency (%)*	**6.4**
Thermal power (BOM)(W_{th})	2000
Thermal efficiency (%)	
Electrical power (BOM) (W_e)	125
Number of GPHS modules	**8**
Total PuO_2 mass (kg)	**5.02**
Total system mass estimate (kg)	**44.2**
Specific power estimate (W_e/kg)	**2.82**

GPHS RTG and MMRTG performance comparison

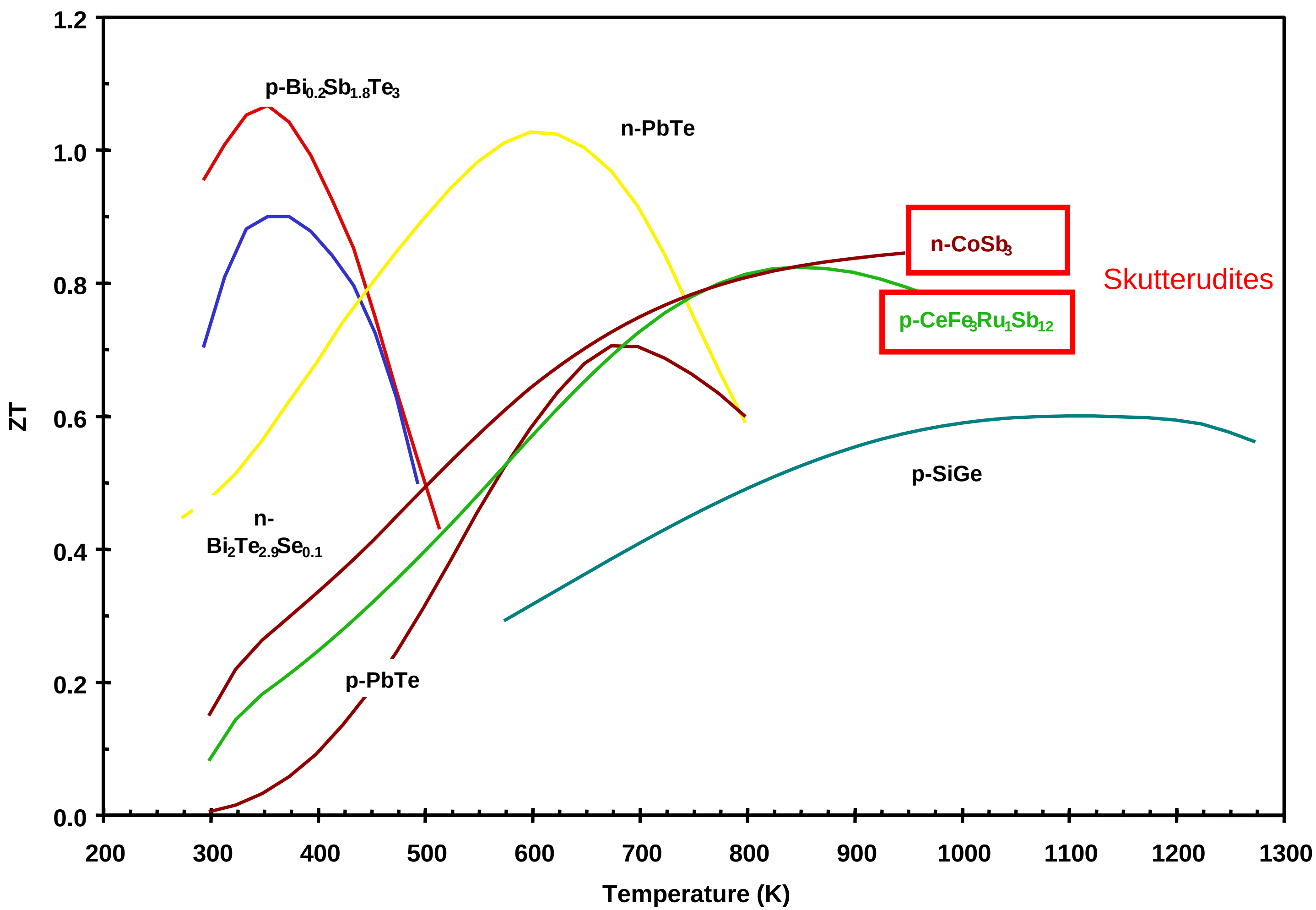
	GPHS-RTG	MMRTG
Operating environment	Vacuum	Vacuum/Planetary
Thermoelectric materials	SiGe	PbTe/TAGS
Hot side temperature (K)	1275	823
Cold side temperature (K)	575	510
Number of GPHS modules	18	8
System efficiency (%)	6.3	6.25
Electrical power (BOM) (W_e)	285	125
Total system mass (kg)	55.5	43.1
Specific power (W/kg)	5.1 uncorrected / <3.4 corrected for Titan 4 & Step 2 GPHS design	2.9

Past, Present and Future RPS Missions

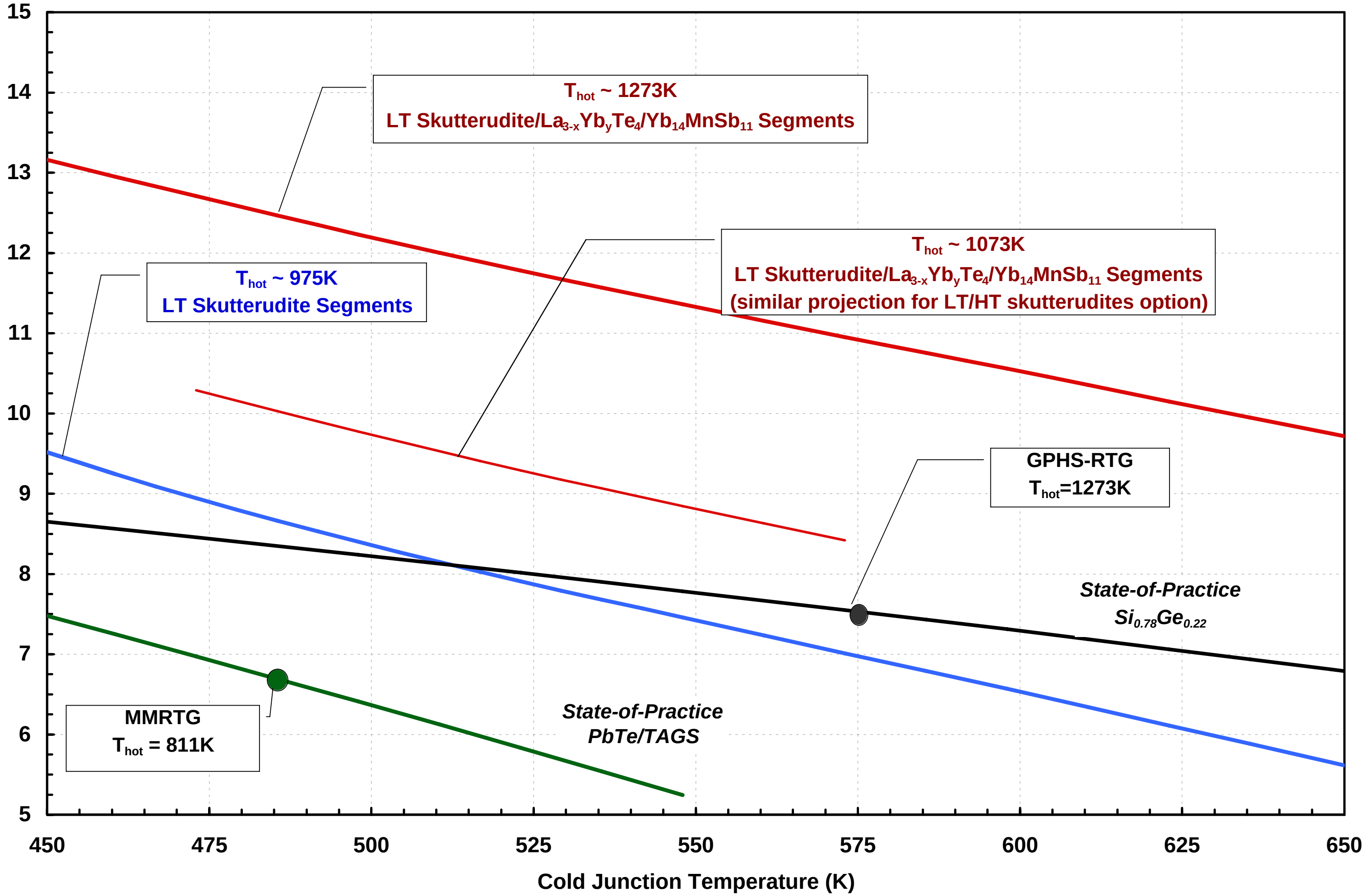
- **Many missions in the past were enabled by RTGs e.g.**
  - **Apollo 12-17 lunar science packages, Pioneer 10 &11, Viking 1 & 2 Landers all used PbTe thermoelectric converter materials in their RTGs (1961 to 1975).**
  - **Voyager 1 & 2, Galileo, Ulysses and Cassini all used SiGe (1976 to 1997).**
- **Mars Science Laboratory (~2009 launch) baseline design assumes the Multi-Mission RTG (MMRTG) using PbTe-TAGS materials (same as Viking 1 & 2 Landers).**
- **Any Europa Orbiter would likely require an RPS**
- ***Future possible missions like Solar Probe, Titan Orbiter and Europa Lander operating in space vacuum and surface missions to Mars and Titan operating in atmospheres could be enabled or enhanced with improved RPS.***

• RPS enabled and/or enhanced past, present and future possible space missions.

ZT values for 1000K skutterudite baseline materials



Couple Efficiency



Key technology challenges

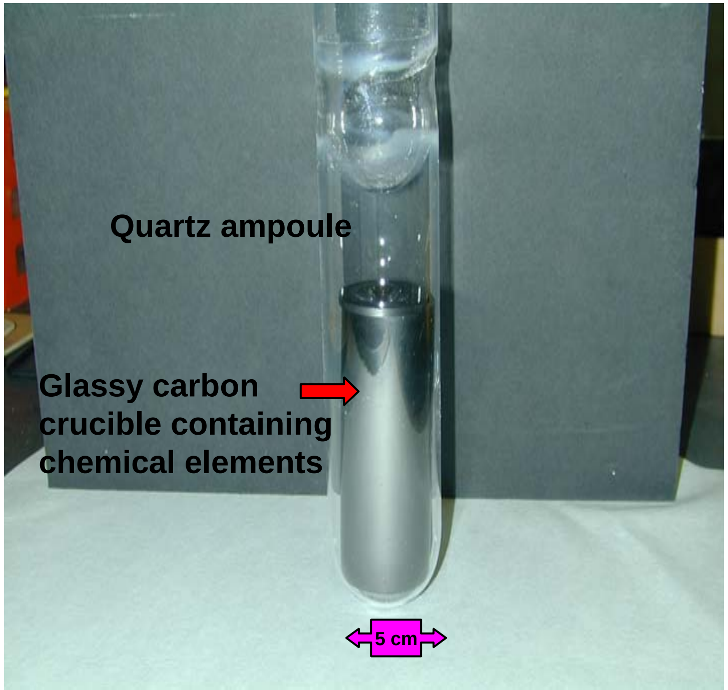
- TE materials synthesis and scale up-processing
- Low electrical contact resistance between TE segments and cold- and hot-shoes
- Demonstrate unicouple performance though testing and modeling
- Lifetime and performance validation
  - Sublimation control
  - Stable thermoelectric properties
  - Unicouple thermal-mechanical integrity

Current Focus

- **Demonstrating skutterudite materials and bond stability and determining degradation mechanisms in order to validate lifetime operation up to 1000K:**
  - **TE materials synthesis scalibility**
  - **Material property measurements as a function of time and temperature**
  - **Sublimation rates as a function of time, temperature, and environment**
    - **Sublimation control: thin metal foil, aerogel, pressurized environment**
  - **Interface diffusion studies**
  - **Couple screening tests and optimization of unicouple configuration in anticipation of lifetime testing**

TE materials - Low-T skutterudites:- Synthesis & Compaction

- **Power metallurgy synthesis for p- and n-type low-T skutterudites**
  - **Melting of elements at ~1200C in BN or glassy carbon crucibles sealed in quartz ampoules under vacuum**
  - **Post-anneal at 700C for 48 hrs**
  - **Ball-milling in steel vials under argon**
- **Hot-pressing**
  - **Graphite dies and plungers**
  - **T~700C and 20,000 psi**

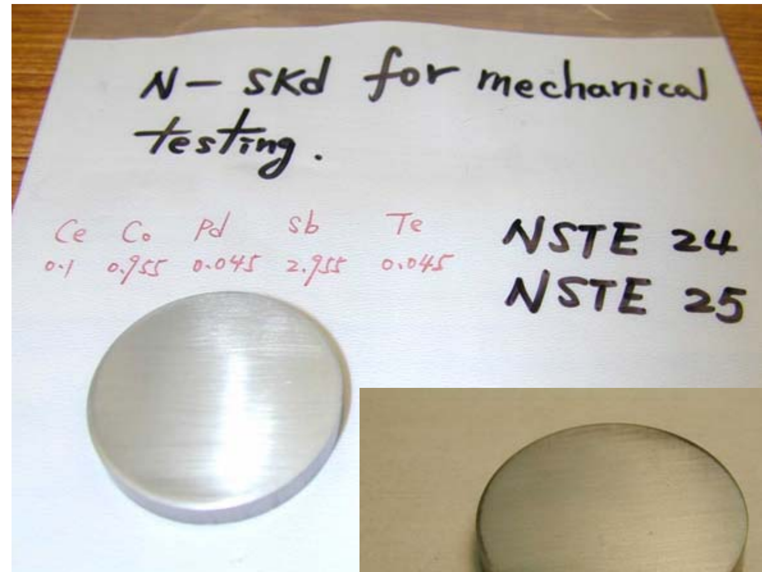


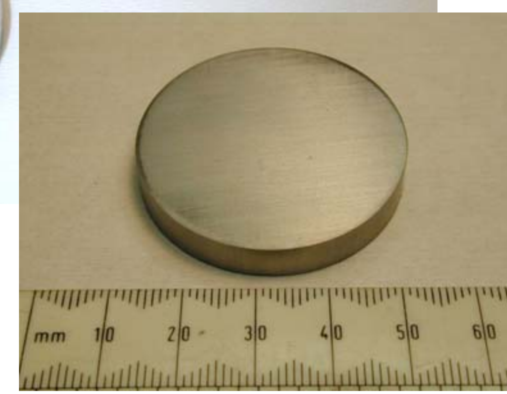
Crucible used for the synthesis of low-T skutterudites

TE materials - Low-T skutterudites:- Pucks production

- **Demonstrated feasibility of hot-pressing large diameter pucks (metallized and non-metallized)**
- **Pucks processing**
  - **Pucks initially diced using a diamond saw**
  - **Also demonstrated that pucks can be cut by wire Electrical Discharging Machining (EDM)**

The powder metallurgy process and pucks processing techniques are compatible for yielding the quantity of legs needed for fabrication of an RTG

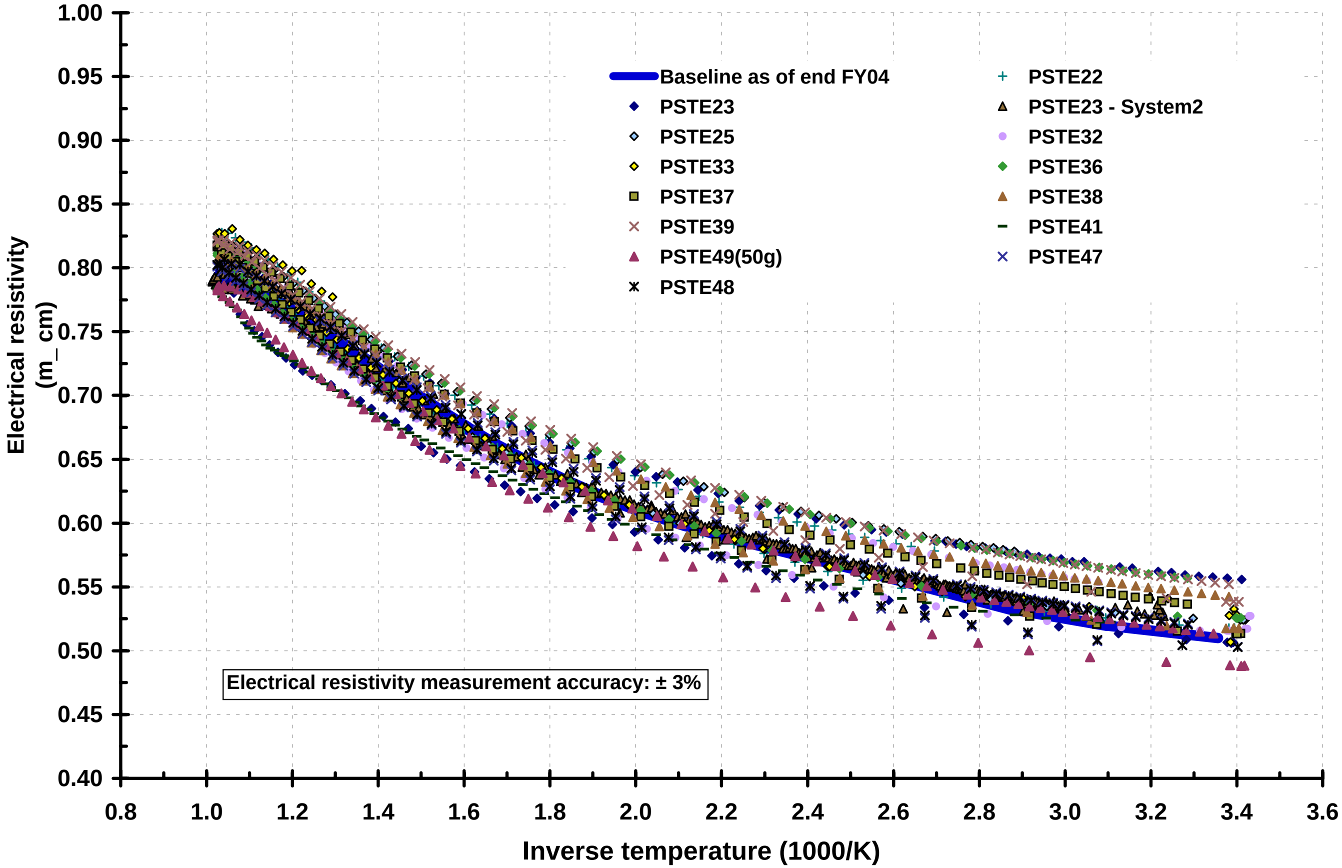




Hot-pressed, 40 mm diameter low-T skutterudites pucks

Low-T skutterudites: TE property reproducibility

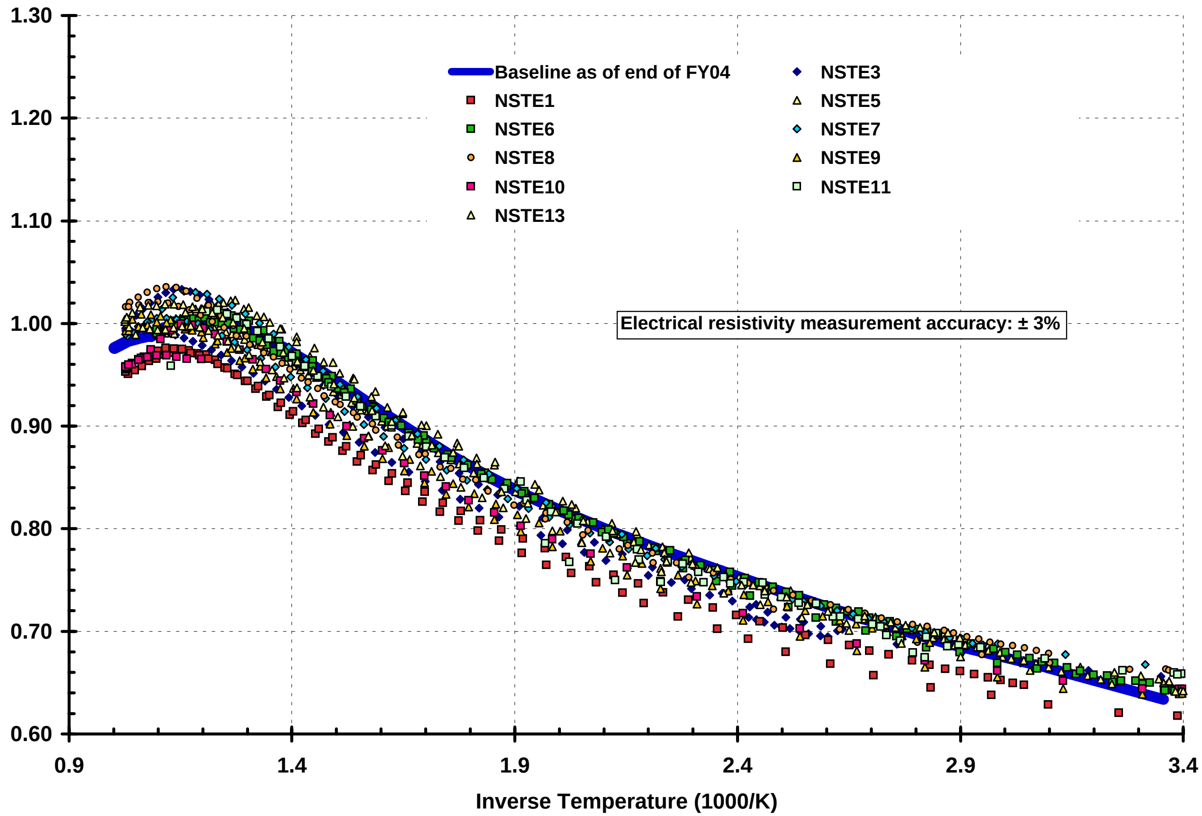
- **Performed electrical resistivity measurements on each p-type batch produced**



Electrical resistivity data is reproducible from batch to batch (within a few % of the end of baseline data)

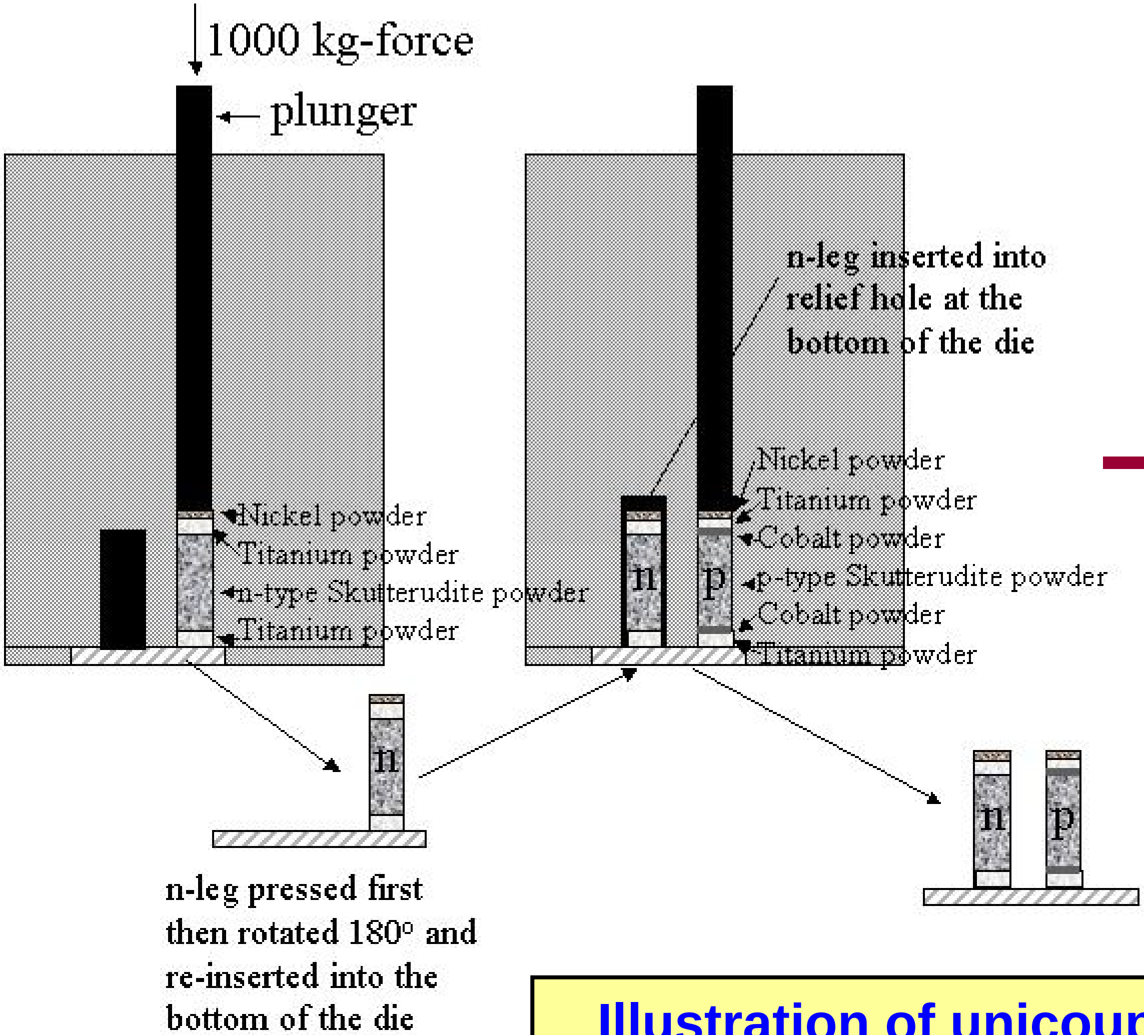
Low-T skutterudites: TE properties reproducibility

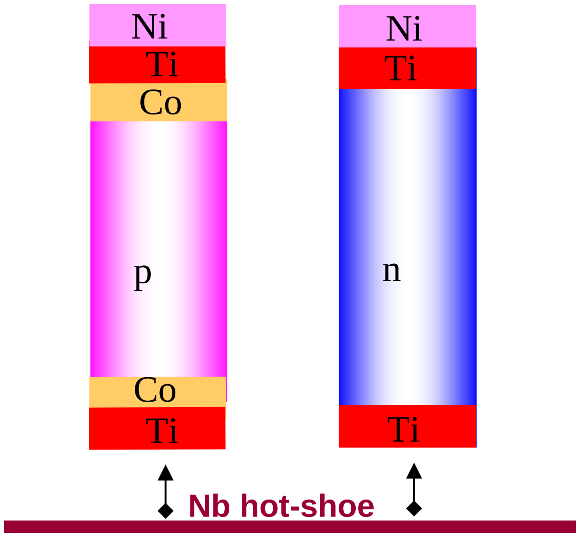
- Performed electrical resistivity measurements on each n-type batch produced



Electrical resistivity data is reproducible from batch to batch (within a few % of the end of baseline data)

Unicouple Fabrication with end of FY04 metallization



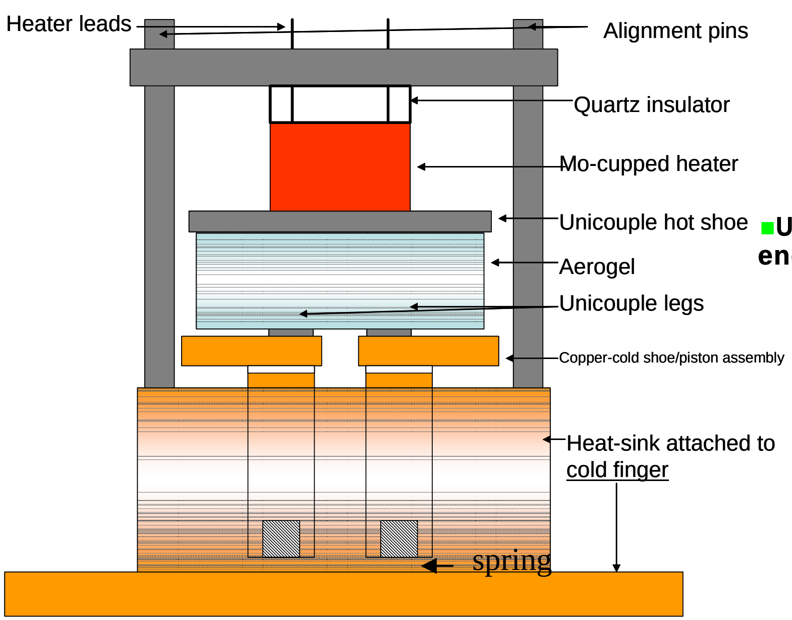


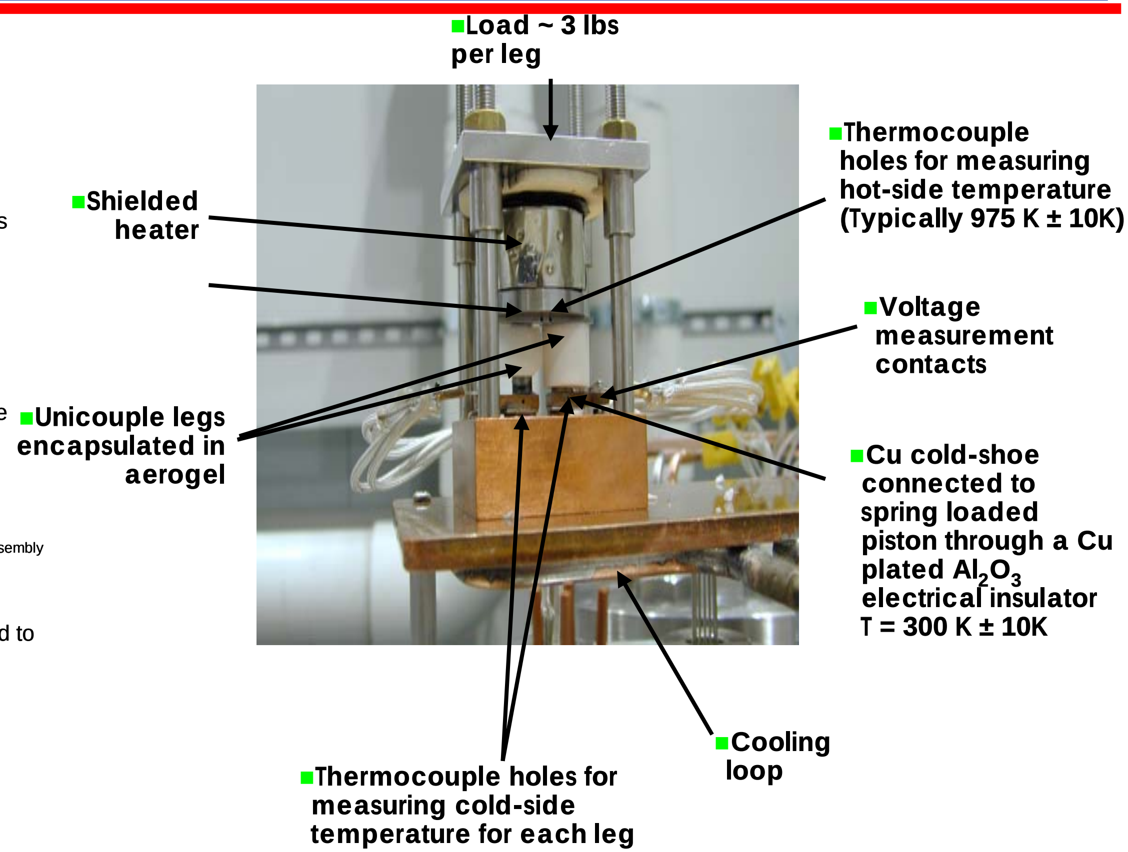
Typical hot-pressing conditions:

1000 kg force for an 8mm bore die, 90minutes, 700C under argon

Illustration of unicouple fabrication process

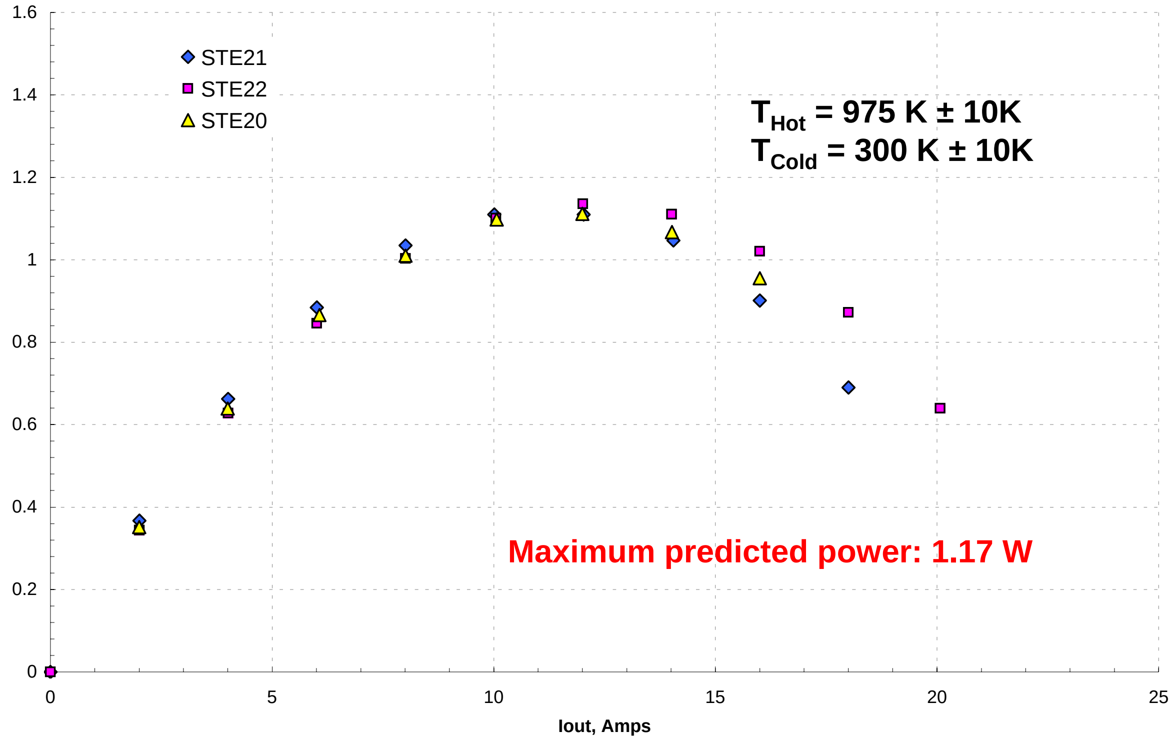
Unicouple performance test fixture





- Performance screening test of spring-loaded low-T skutterudite unicouples
  - In-gradient testing with T_{Hot} = 975 K ± 10K and T_{Cold} = 300 K ± 10K
  - Vacuum environment (10^{-6} Torr)
  - Power output vs. load current at constant hot-shoe temperature

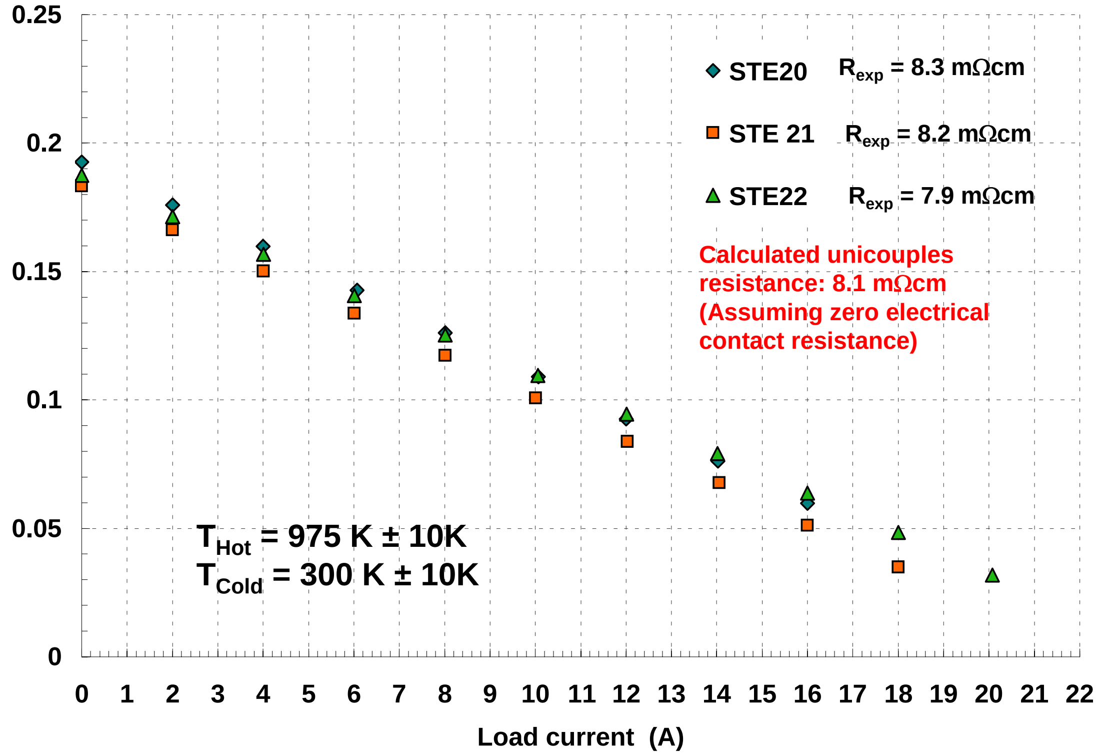
Unicouple performance testing



Beginning of Life Power Output for unicouples STE20, 21, and 22

- All three unicouples generated BOL peak power within 1-3% of predicted values calculated from the TE properties and the hot-side and cold-sides operating temperatures
- The deviation from the predicted value is well within the measurement errors for the TE properties

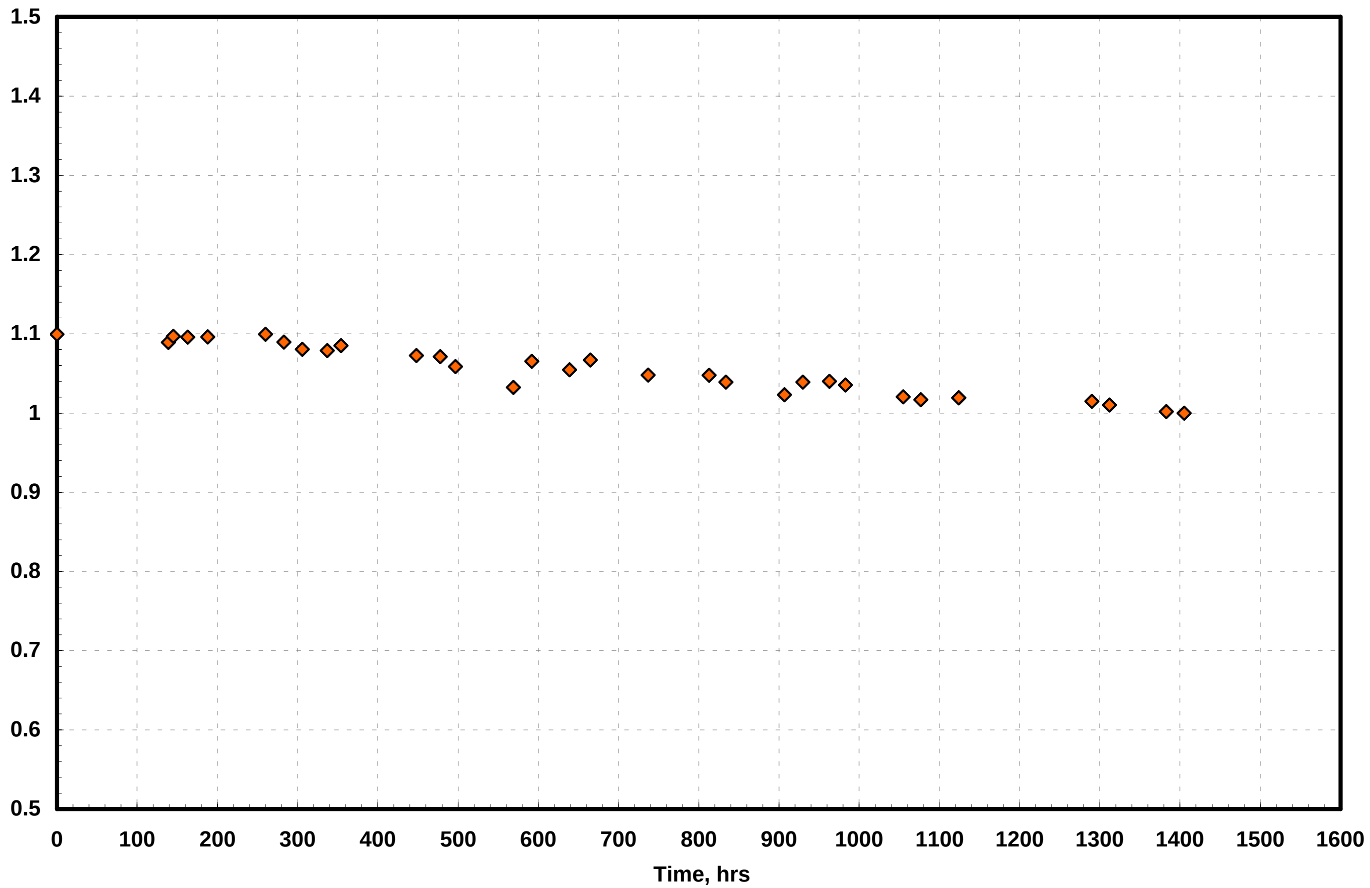
Unicouple performance testing



Beginning of life I-V curves for STE20, 21, and 22

- All three unicouples calculated resistance (from the I-V curves at constant temperature) is within 1-3% of predicted values calculated from the TE properties and the hot-side and cold-sides operating temperatures; this result also confirms that the different unicouple junctions have negligible electrical contact resistance
- The deviation from the predicted value is also well within the measurement errors for the TE properties
- Unicouple voltage output is also within 1-3% of predicted values calculated from the temperature dependent Seebeck data

Initial unicouple performance/Life testing



- Life testing of low-T unicouples has been initiated
  - Evaluate degradation mechanisms
  - Optimize as needed to achieve performance degradation goals

Lifetime performance demonstration elements

THERMOELECTRIC PROPERTIES

Examples :
- SiGe: dopant precipitation
- Fine grained SiGe: grain growth
- TAGS : compositional change

Testing:
- Coupons

Impact:
- Change in efficiency, P output

Solution:
- Composition, doping control

MATERIALS SUBLIMATION

Examples :
- SiGe: Si & Ge
- TAGS, PbTe: Te, Se, Ag, Sb
- Skutterudites : Sb

Testing:
- Coupons

Impact:
- A/l, porosity, contact resistance, mechanical failure

Solution:
- Encapsulation, coatings
- More refractory materials

THERMAL INSULATION

Examples :
- Si in MFI

Testing:
- Unicouple

Impact:
- Shorting
- Contamination

Solution:
- Processing and engineering control

THERMO-MECHANICAL INTEGRITY

Testing:
- Unicouple

Impact:
- Contact resistance
- Mechanical failure

Solution:
- Device engineering/modeling

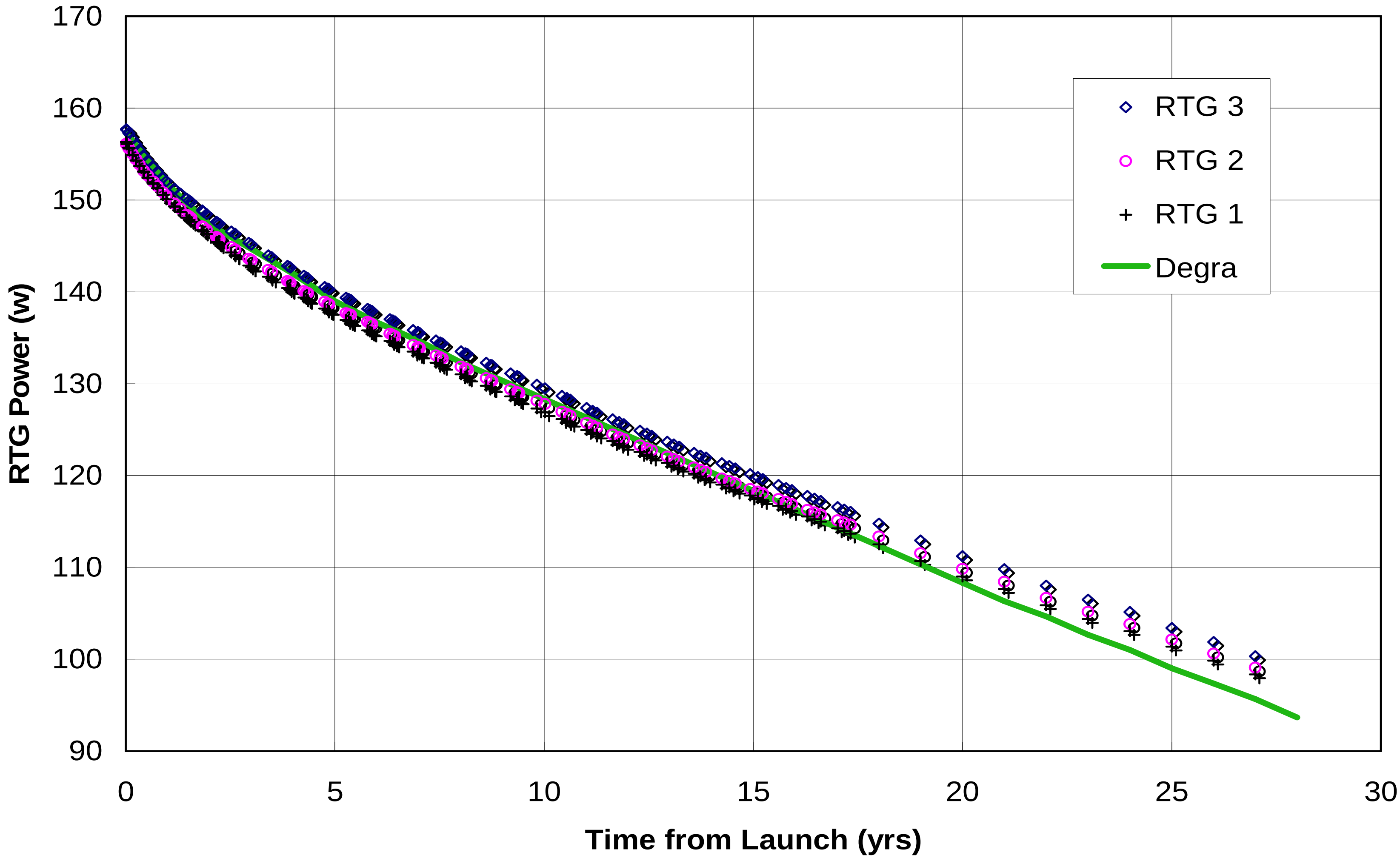
LIFETIME MODEL

FUEL DECAY

Main RTG degradation mechanisms

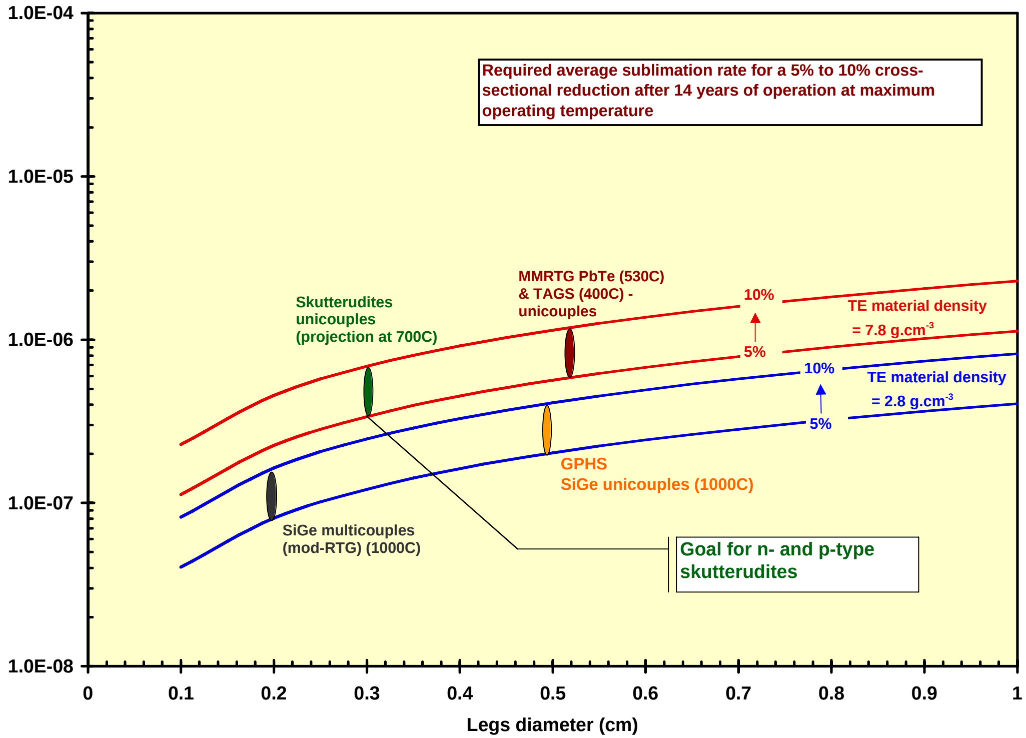
- **Both GPHS and MMRTG show about 22% power output degradation over 14 years of operation (~ 1.6% per year)**
- **Main degradation mechanisms**
  - **Fuel (PuO_2) decay**
    - **~ 0.8% thermal input decrease per year**
  - **The thermal input decrease drives T_{hot} and the ΔT across the TE converter down, resulting in a conversion efficiency decrease and a power output decrease of ~ 0.5% /year**
  - **Balance of power output decrease (~0.3%/year) is due to:**
    - **Change in properties of thermoelectric materials**
    - **Sublimation of TE materials resulting in geometry changes of the TE legs (typically a cross-sectional reduction)**
    - **Electrical contact resistance changes over time**
  - **Degradations rates for materials and couples related mechanisms can be evaluated at operating and accelerated temperatures to model and predict RTG power output vs. time**

Voyager 1 Power Output vs. Time



Sublimation suppression

– Demonstrate that desired sublimation rates (5 x 10^{-7} $g/cm^2/hr$) can be achieved for coated/encapsulated low-temperature skutterudites coupons up to 975K over time



Calculated required sublimation rates (in $g/cm^2/hr$) to keep the cross-sectional reduction of the TE elements between 5 and 10% after 14 years of operation at maximum operating temperature

Detailed Methodology for Sublimation Rate Measurement

BOL sublimation rate measurement with thermogravimetric analysis (TGA) system (FY01-FY05) → **Coupon life test with minimite station FY05**

- Beginning of Life (BOL) Sublimation rates were measured in-situ with TGA
- Detection limit of TGA is ~ 1×10^{-5} g/cm^2hr with hours operation
- Baseline is measured first for the calibration of real data
- TGA is not appropriate for long operation, therefore another method was employed for life tests in FY05

Beginning of Life

- Coupons were heated in a tube furnace under dynamic vacuum
- Weight change was measured every week after cooling coupons and breaking vacuum
- Quartz cup and Mo basket were used to transfer coupons safely in and out of ampoules during life tests

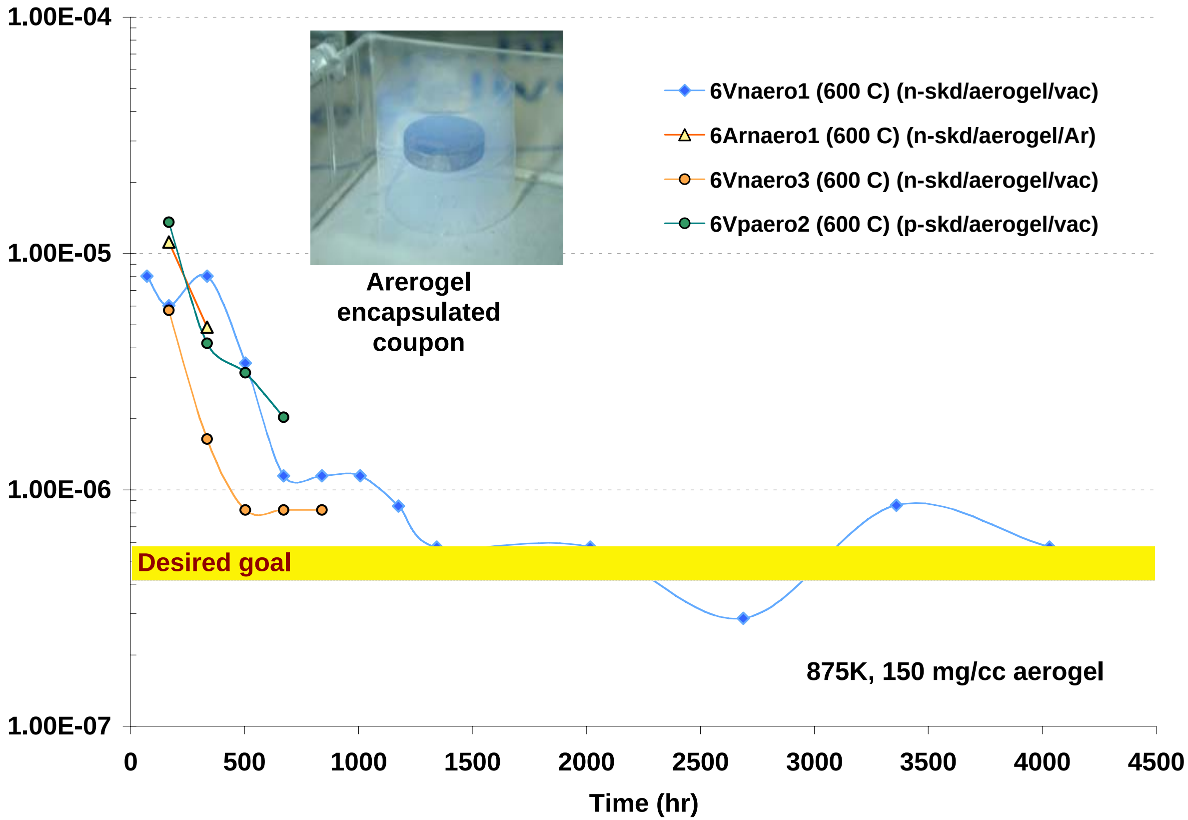
Months to Years

Sublimation Studies Summary

- Identified Sb as the main product subliming form skutterudite materials
- Characterized the beginning of life sublimation rates for bare low and high-T skutterudite materials
- Identified promising Sb sublimation suppression techniques
  - Aerogel encapsulation
  - Thin-film metallic coating
- Developed methodology and techniques for life testing sublimation rates
- Developed a two-step hot-pressing process to allow for improved uniformity of TE legs thin-foil encapsulation
- Developed aerogel composite:
  - Overall density of 150 mg/cc (75 mg/cc silica aerogel, 20 mg/cc fumed silica, and 55 mg/cc quartz powder)
  - Lower shrinkage than that for pure silica aerogel

BOL rates	Un-encapsulated ($g/cm^2/hr$) (vacuum)	100mg/cc aerogel ($g/cm^2/hr$) (vacuum)	Ti + Mo coated (vacuum)	150 mg/cc aerogel composite ($g/cm^2/hr$) (vacuum)
675 K	Not detectable	Not detectable	Not detectable	Not detectable
775 K	5.31×10^{-4}	Not detectable	Not detectable	Not detectable
875K	5.16×10^{-3}	4×10^{-4}	Not detectable	Not detectable
975 K	2.15×10^{-2}	1×10^{-3}	Not detectable	10^{-5}

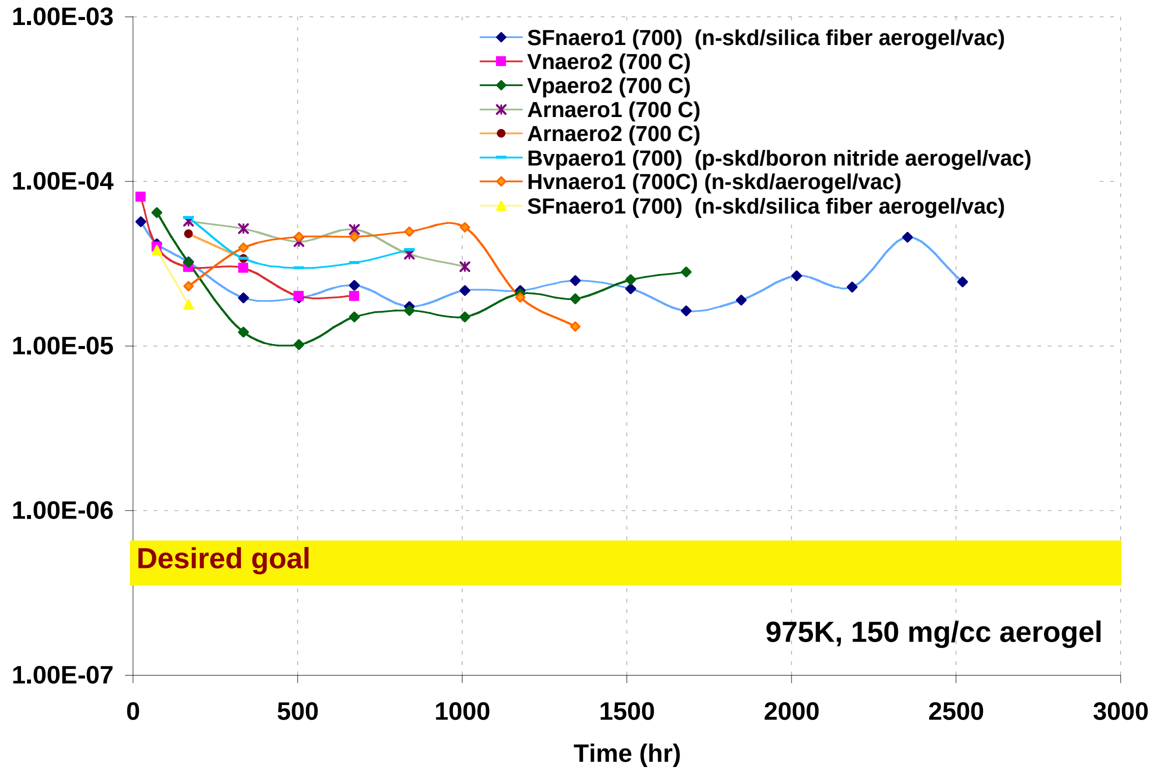
Sublimation Rates Life Tests at 875 K n- and p-type low-T SKD Aerogel Encapsulated Coupons



- Demonstrated that the desired sublimation rate ($<5 \times 10^{-7}$ g/cm^{2}hr) for 14 years of operation can be achieved up to 875K for aerogel-encapsulated low-T skutterudites after up to 4000 hours of testing

- Initial data shows no further decrease in sublimation rate for 1 atm Ar vs. dynamic vacuum

Sublimation Rates Life Tests at 975K n- and p-type low-T SKD Aerogel Encapsulated Coupons

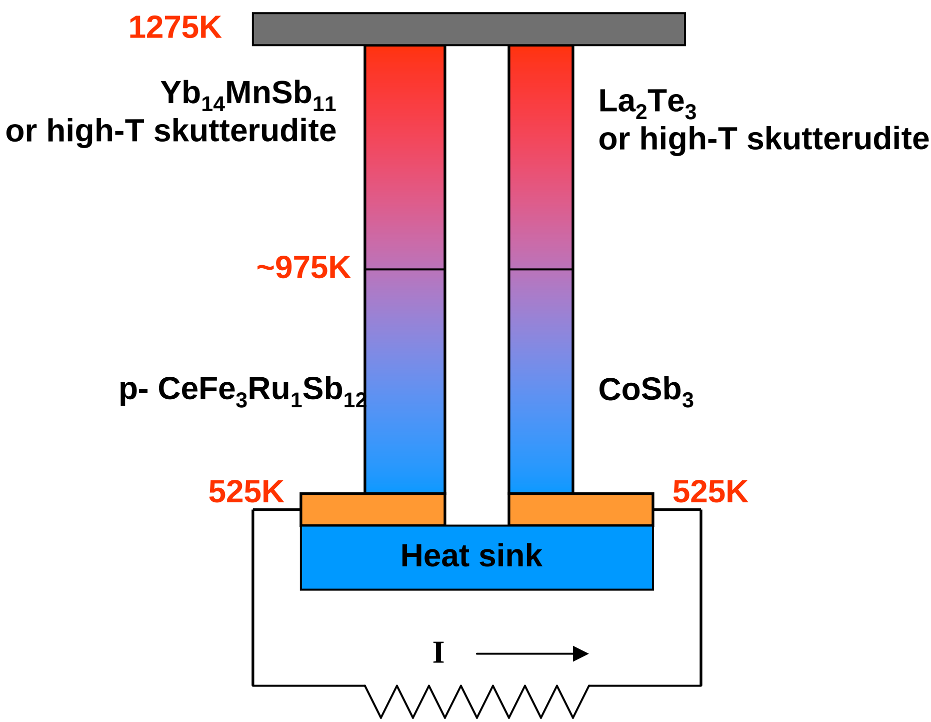


- Results show that sublimation rates are two orders of magnitude too high compared to desired rates (5 x 10^{-7} $cm^2/g/hr$) (with current best 150 mg/cc aerogel)
- Initial data shows no further decrease in sublimation rate for 1 amt Ar vs. dynamic vacuum
- Sublimation rates data acquired to date on aerogel encapsulation and thin-film coating suggest however that a combination of both is likely to yield the desired rates up to 975K

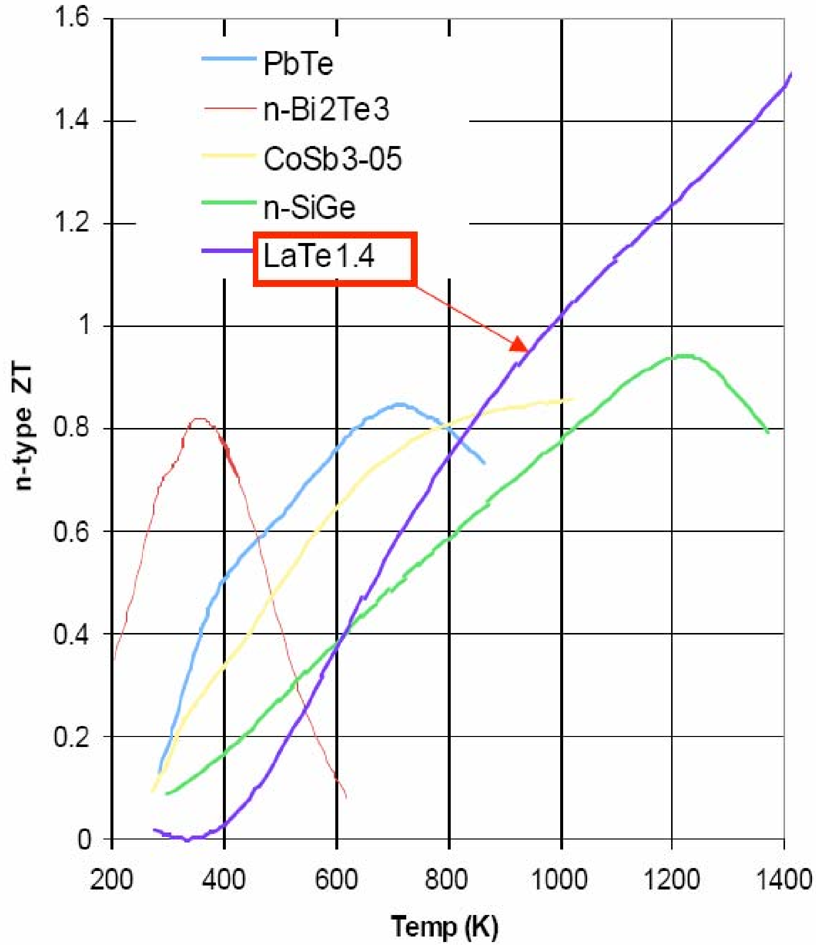
Advanced RTG Requirements

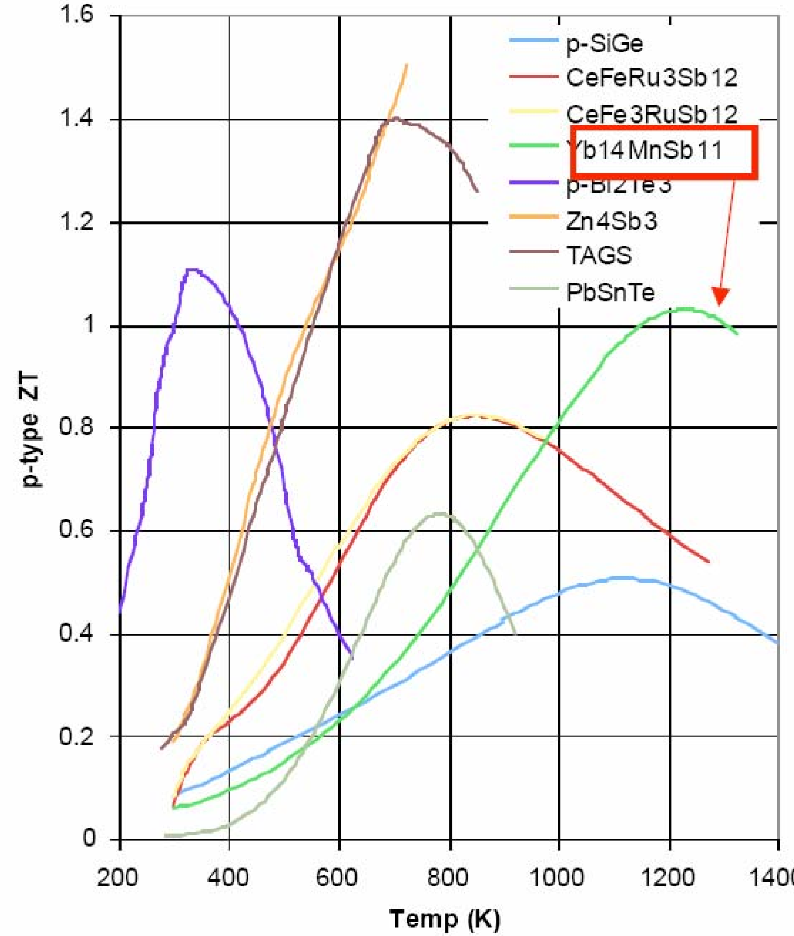
- **NASA Advanced RTG Requirements:**
  - Specific Power: At least 6 W/kg
  - Lifetime: At least 14 years with less than 22% degradation
  - Environment: Deep space with $0.3g^2/Hz$ random vibration
  - Heat Source: Step 2 GPHS

- **Requires to increase couple efficiency**
  - Use segmented unicouples
  - Low-T skutterudites as low temperature segments
    - p- $CeFe_3Ru_1Sb_{12}$ and n-$CoSb_3$
  - High-T segments (up to 1275K):
    - P: Zintl $Yb_{14}MnSb_{11}$ or high-T skutterudite
    - N: La_2Te_3 or high-T skutterudite

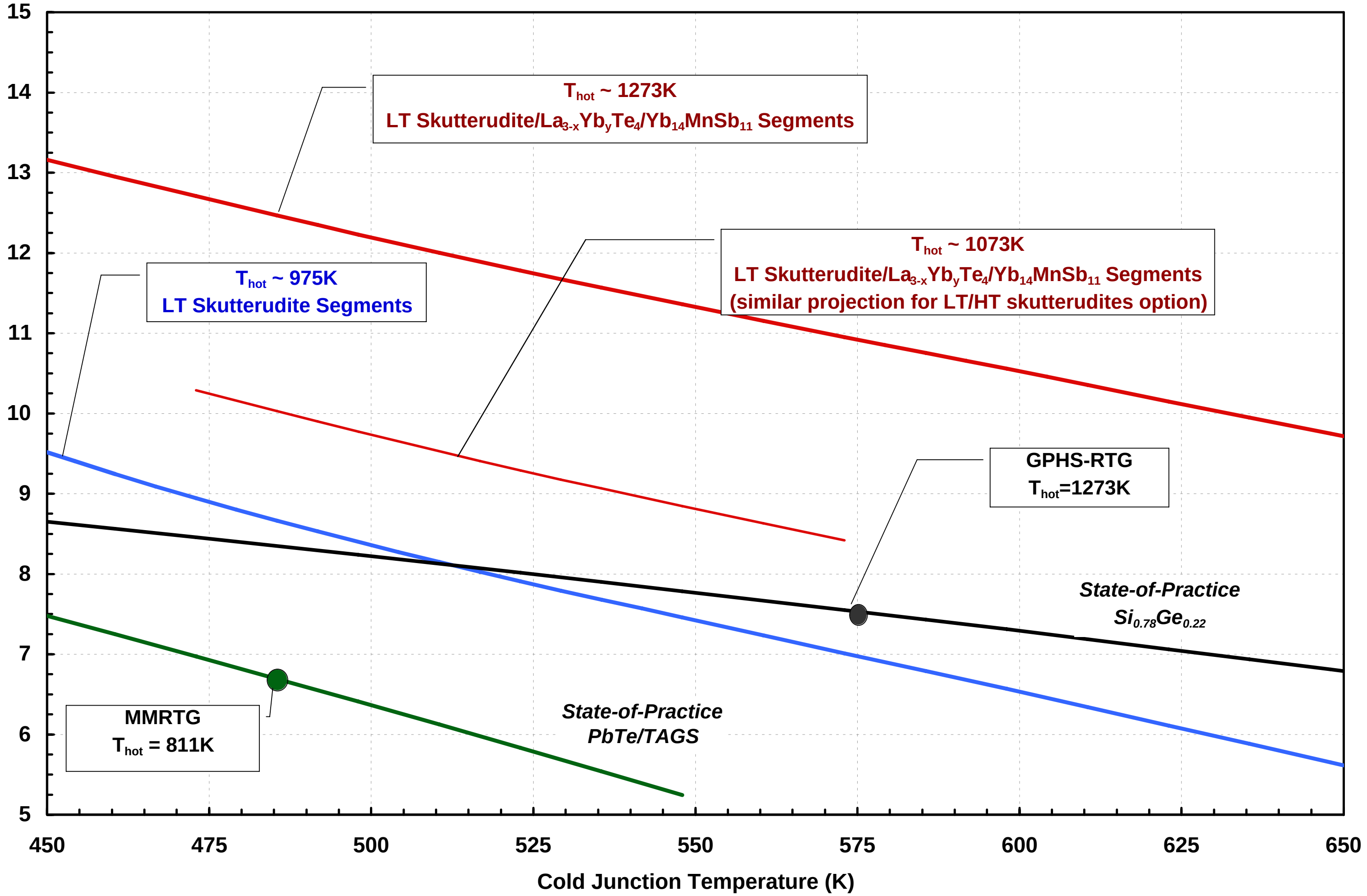


Best TE Materials to Date





Couple Efficiency



Summary

- **Summary**
  - **Many missions in the past were enabled by RTGs**
  - **Some future deep space and planetary missions would benefit from higher performance RPS**
  - **Developed first generation low-T (up to 700C) skutterudite-based unicouples**
  - **Initiated life studies to qualify skutterudite materials and technology**
  - **Second generation advanced thermoelectric materials and technology is currently being developed to further increase RTG performance**

- **Acknowledgements**
  - **NASA Science Missions Directorate for funding**