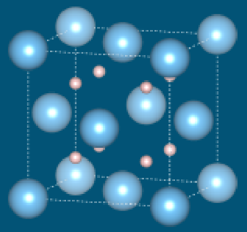
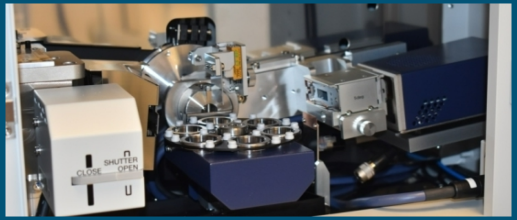
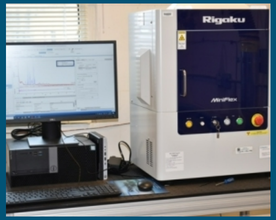
SAND2022-2282C

Sandia National Laboratories

Exploring the Sub-Stoichiometric Titanium Hydride (δ-TiH_x) Phase Space







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TMS 2022 Annual Meeting and Exhibition

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U.S. DEPARTMENT OF ENERGY

NNSA

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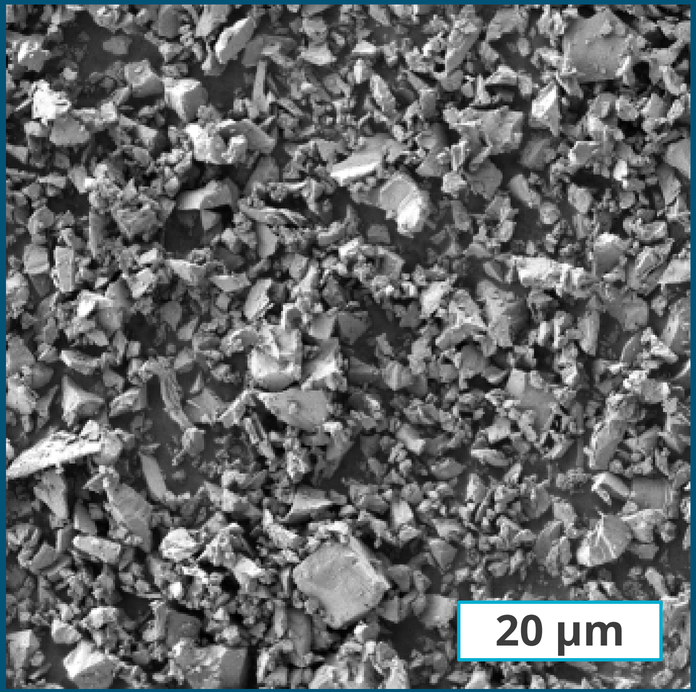
Titanium hydride applications

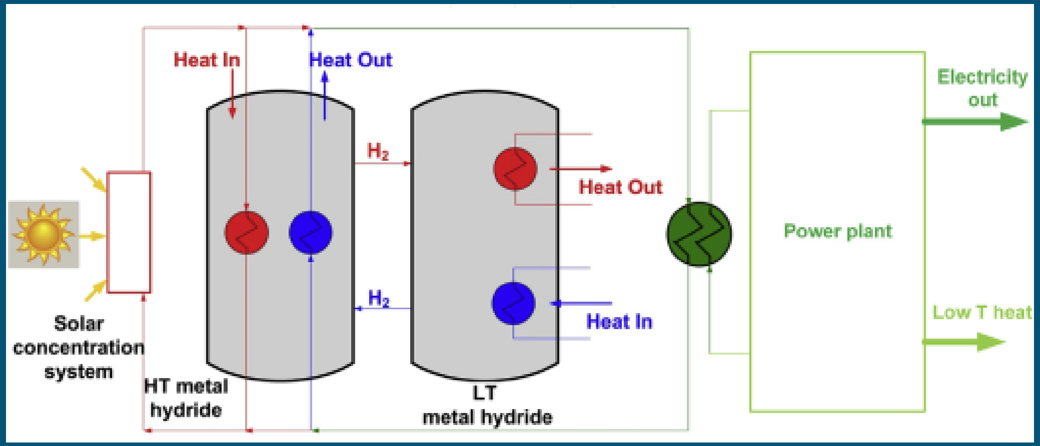
- Intermediate in HDH Ti powder production
- Blowing agent for metal foam
- Powder metallurgy and additive manufacturing
- Hydrogen storage
  - Energy applications
  - Release of high-purity hydrogen
- Model system
  - Similar concerns with other metal hydrides

Need for precision hydrogen quantitation in hydrogen-rich (up to several wt. %) materials.



TiH_2 powder

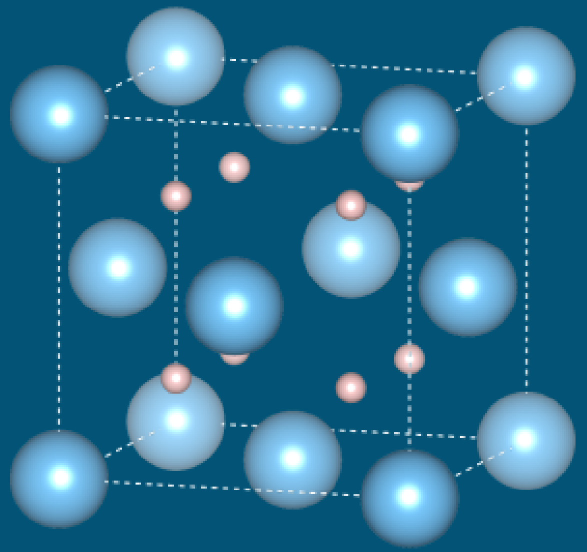

Via Wikimedia Commons , user Stehfun



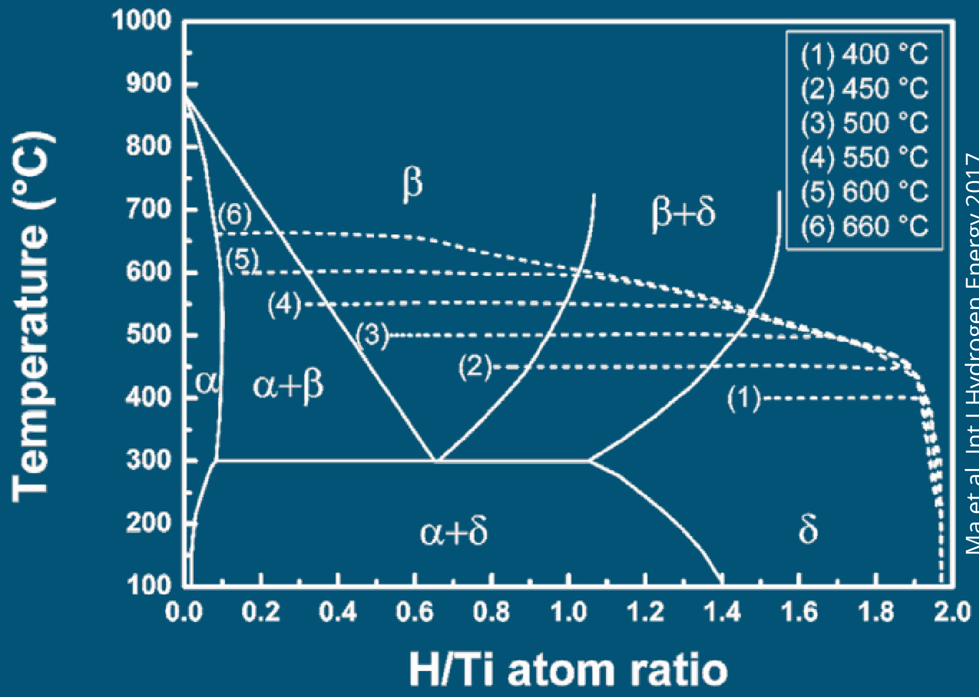
Corgnale, et al, Int J Hydrogen Energy 2016

H-Ti Phases

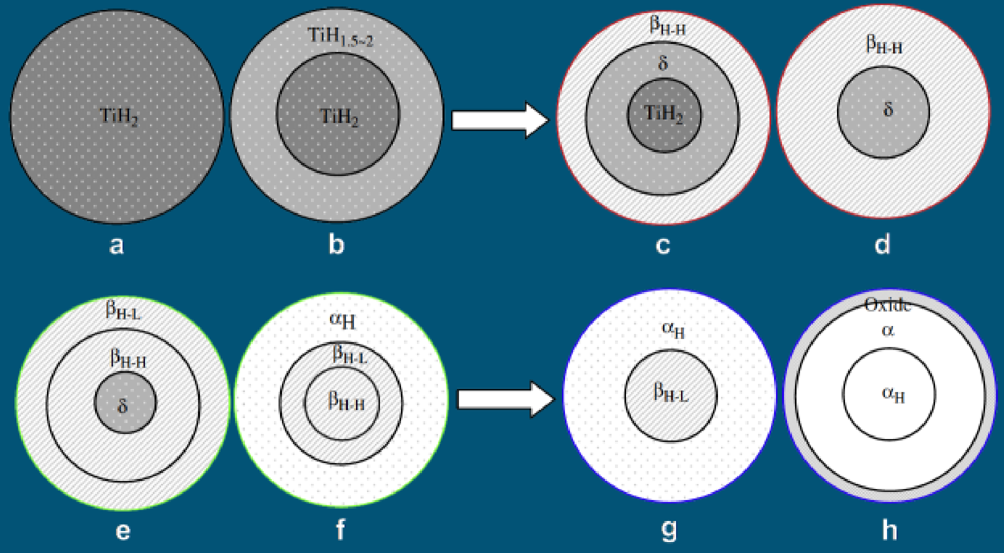
- Phases present: α-Ti, β-Ti, and δ-TiH_x
  - Potentially γ- and ε-TiH_x
  - Coexistence of multiple phases
- Significant capacity to absorb oxygen
- Hydrogen release starting at 250 to 350 ˚C



δ-TiH_2 Unit cell rendered in VESTA



Ma et al, Int J Hydrogen Energy 2017.



Wang et al, Int J Hydrogen Energy 2009.

Important to quantify phases present and hydrogen content.

Relevant analytical techniques

Heating + desorbed gas analysis

- Optical, pressure, or mass spec (MS) detection
- Inert gas fusion (LECO)

Heating + gravimetric analysis

- Thermogravimetric analysis (TGA), quartz crystal microbalance

Combined thermal techniques

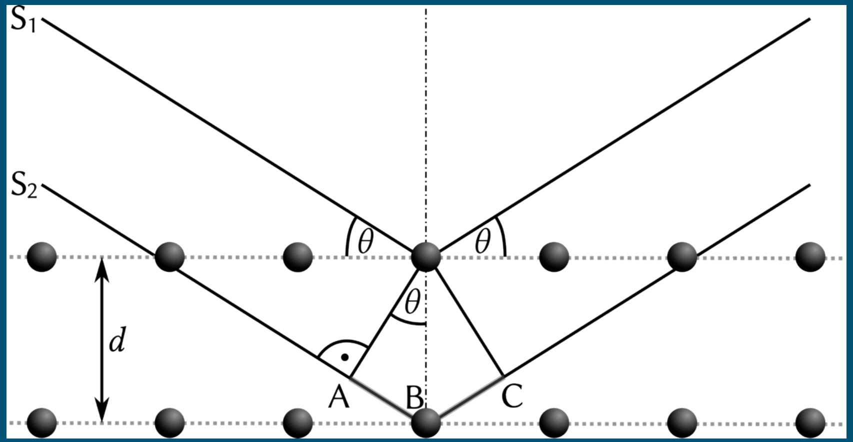
- Improved accuracy by comparing different data
- Simultaneous TA (STA Netzsch TGA-MS)

X-ray Diffraction (XRD)

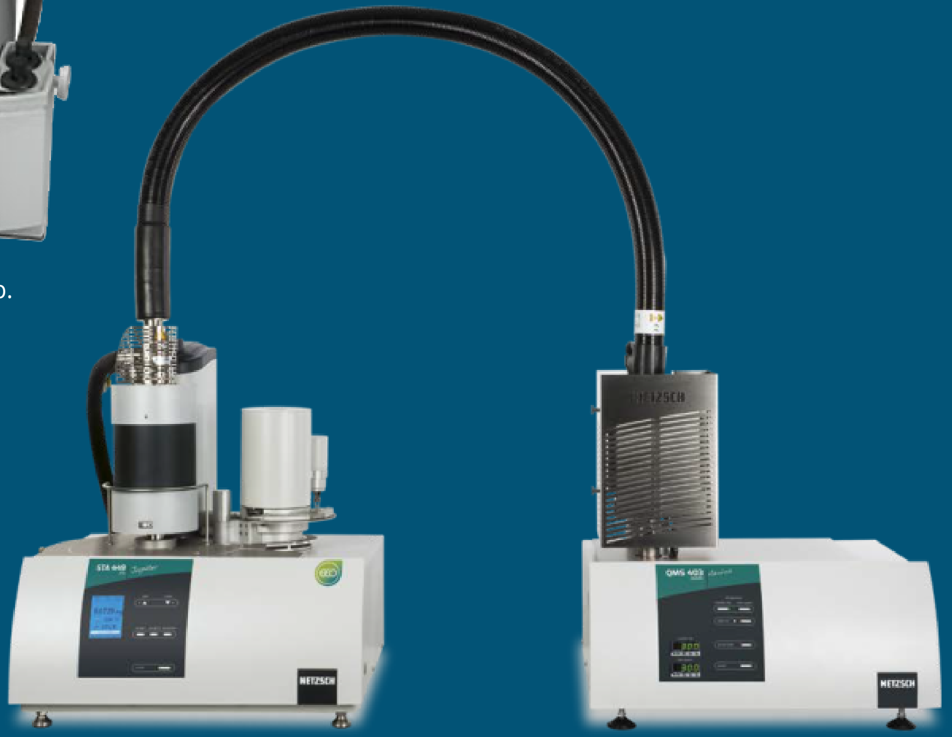
- Fast and nondestructive

How do we verify both hydrogen content and phase purity?

LECO Corp.



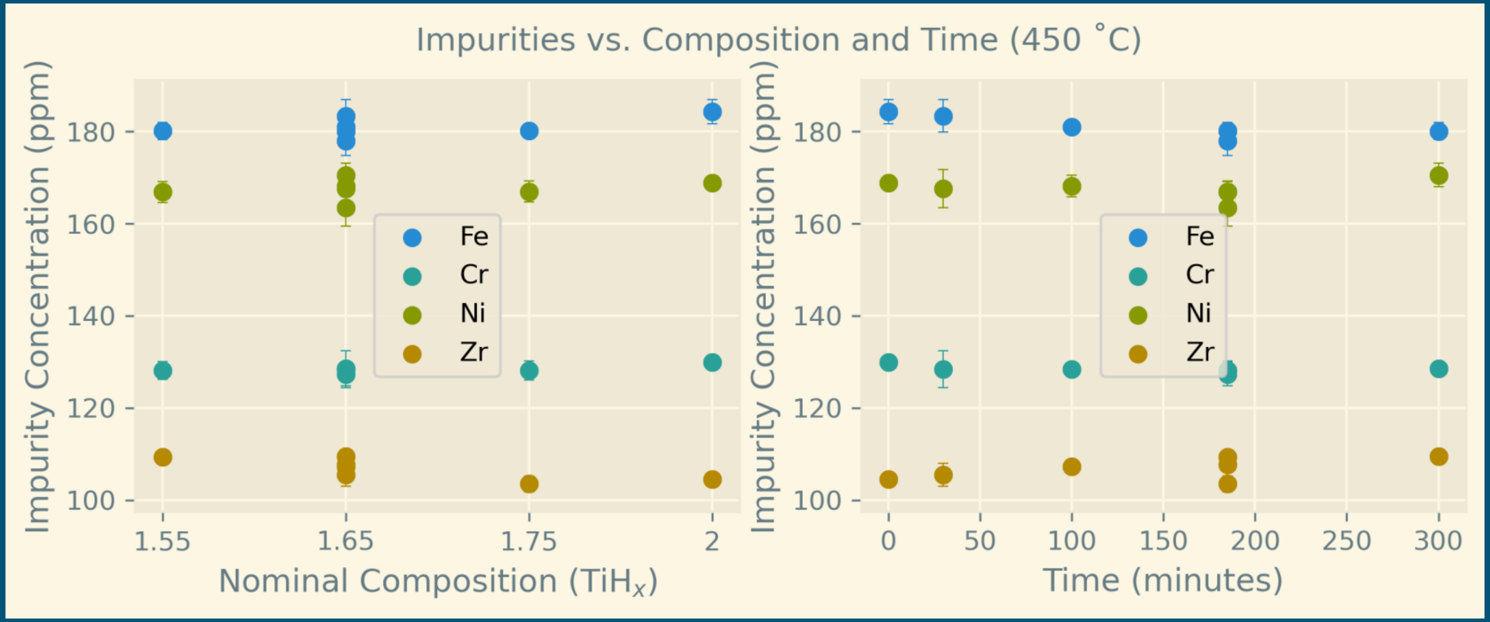
Via Wikimedia Commons , user Freundchen

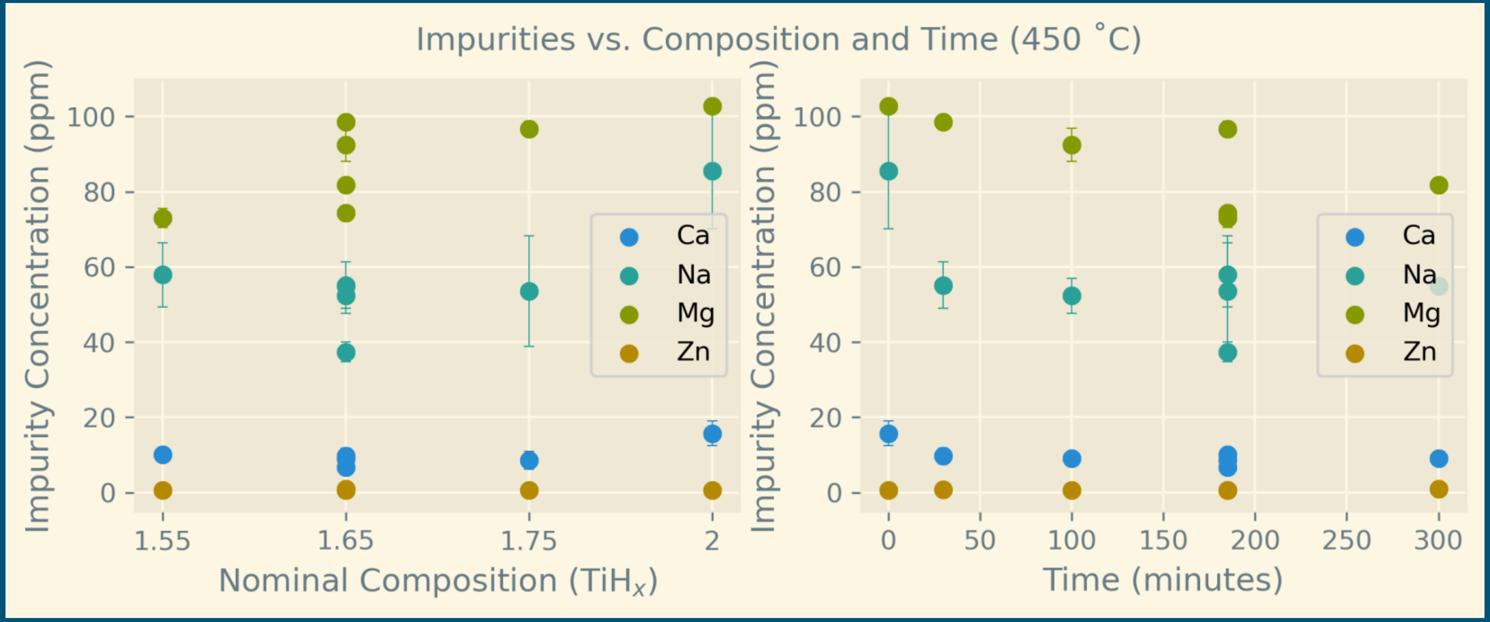


Netzsch Group

Chemical Analysis (ICP-OES and –MS)

- Commercial (Alfa Aesar) powder
- Nominally TiH_2
- Total metallurgical impurities ≈ 600-700 ppm (0.06-0.07 wt. %)
- Consistent fractions of Fe, Cr, Ni, and Zr
  - Likely associated with stainless steel vessels used in synthesis
- Decrease in Mg, Na, Ca, Zn
  - Likely associated with Ti synthesis processes

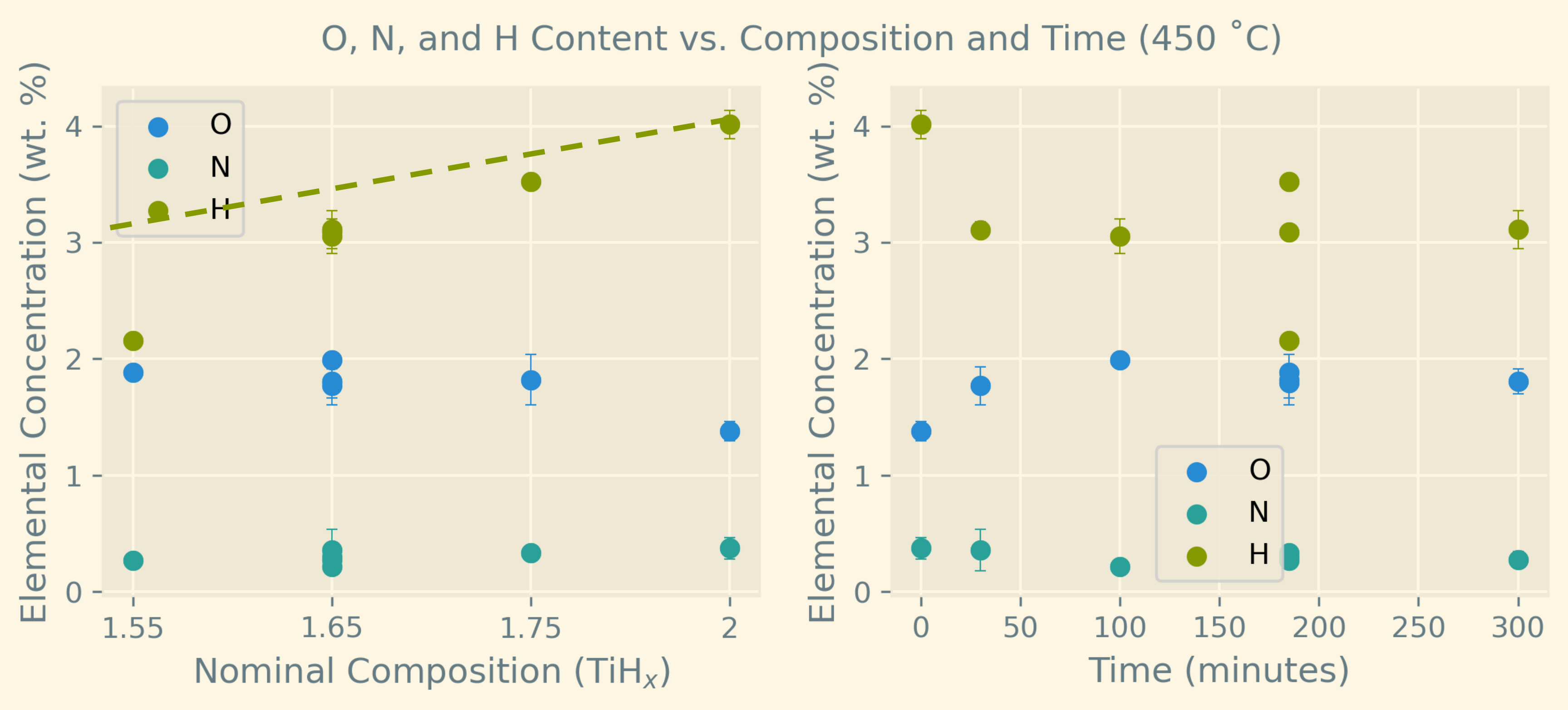




Results consistent across samples and representative of TiH_x.

Inert Gas Fusion (LECO Elemental Analyzer)

- Process:
  - Thermal desorption
  - Reaction with oxygen
  - IR detection cells
- Typically calibrated and used in the range of ≈ 1 to 100 ppm. (0.001 to 0.01 wt. % H)
- Capable of extended range with proper calibration (Babikhina, et al, *Metals* 2018.)
- Commercial "TiH_2" may actually be $TiH_{1.8X}$ or $TiH_{1.9X}$
  - And may contain significant O!
- Calibrated here with ZrH_2, TiH_2, MgH_2 (≈ 2, 4, and 8 wt. % H)

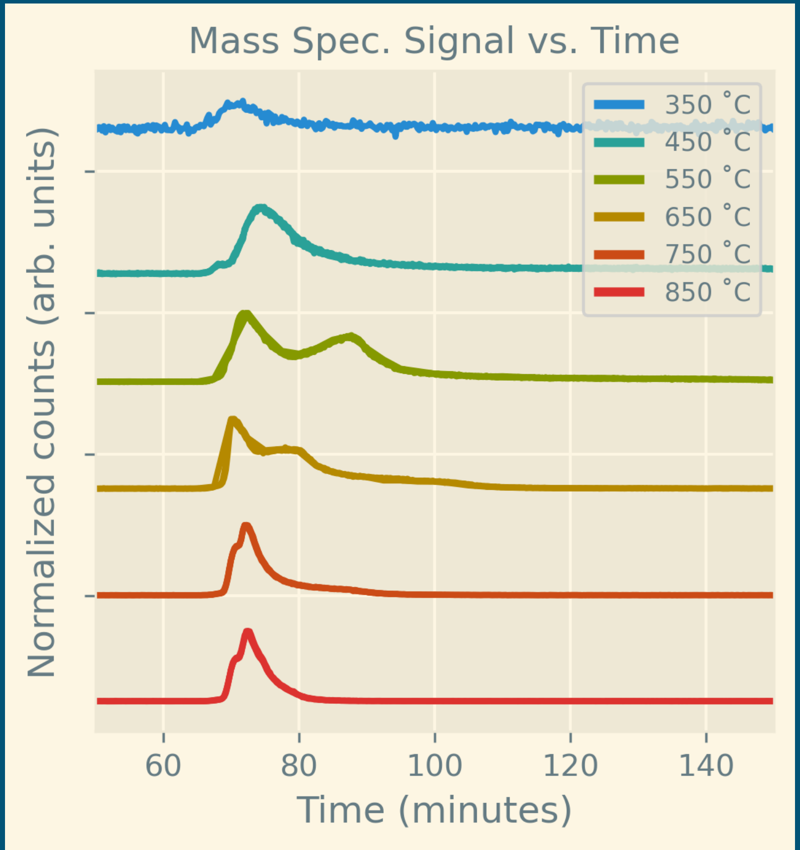


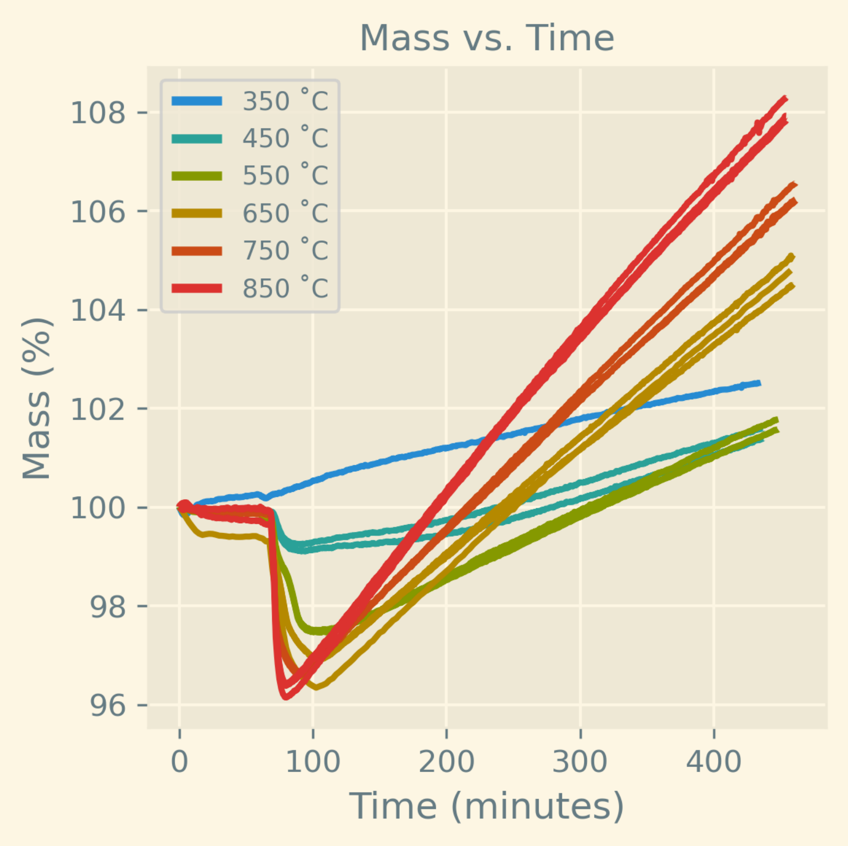
	TiH_2		$TiH_{1.75}$		$TiH_{1.65}$		$TiH_{1.55}$	
	Meas.	Theory	Meas.	Theory	Meas.	Theory	Meas.	Theory
H (Wt. %)	4.01	4.04	3.52	3.55	3.09	3.36	2.16	3.16

Delivers promising, consistent results but certified hydrogen reference materials are not available.

TGA-MS

- Process:
  - Thermal desorption
  - Continuous TG and MS detection
- MS signal is highly precise and accurate, but sample introduction causes uncertainties
  - Gas flow rate
  - Ionization source drift over time
  - Quantitative mass loss possible, but mostly in specialized instruments (Behrens, *Rev Sci Instr* 1987.)
- TG signal must be scrutinized
  - Impurities in carrier gas
  - Heating rate and hold time

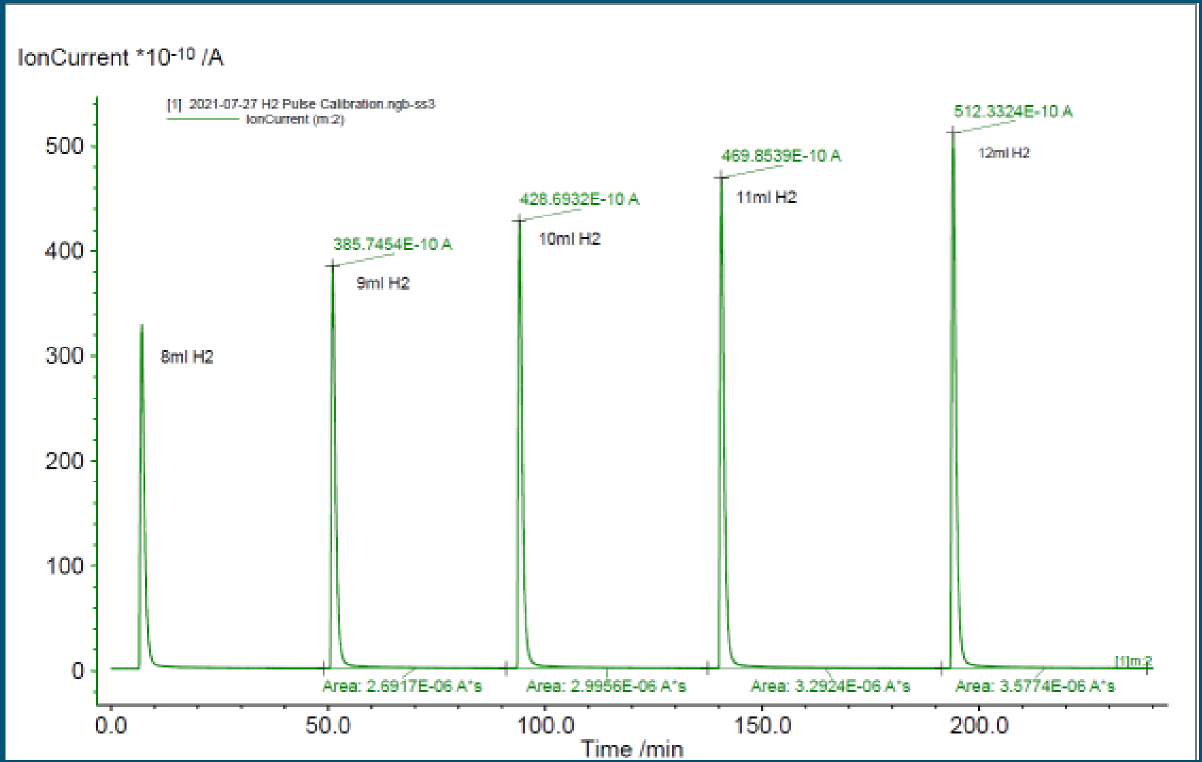




Abundance of useful information but results cannot be taken at face value.

TGA-MS

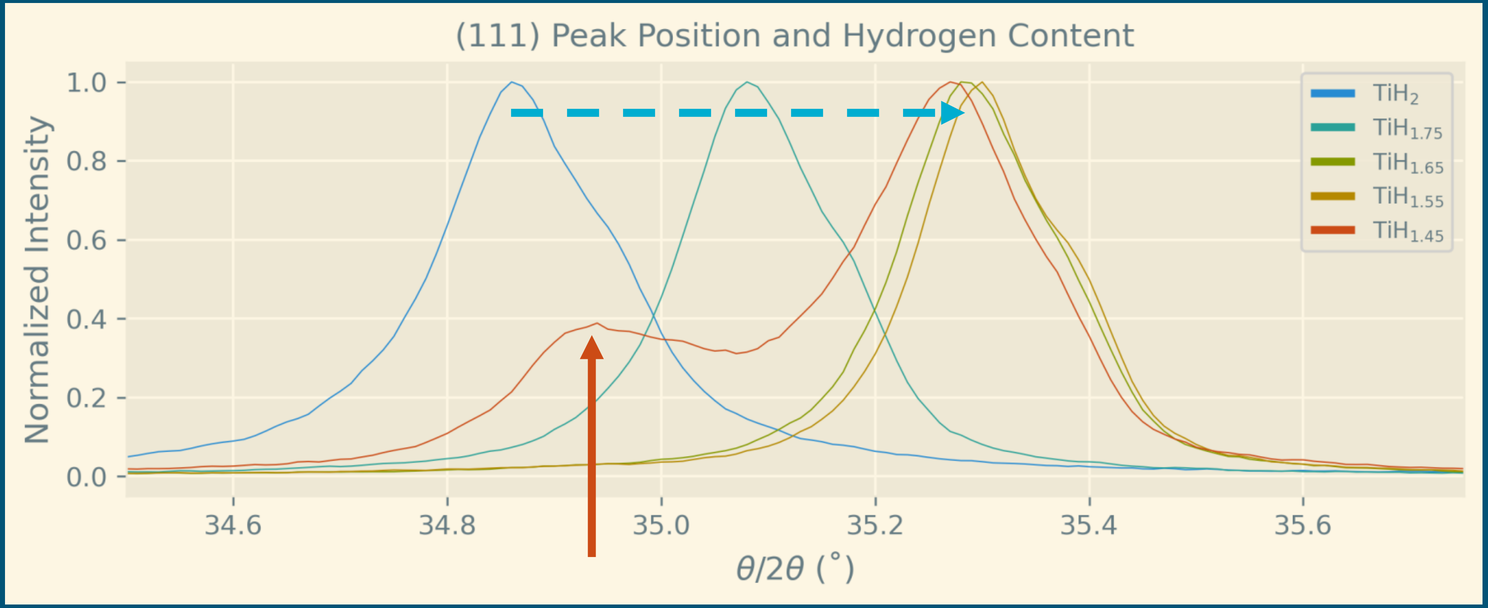
- TG
  - Linear correction often sufficient if hydrogen loss rate is high enough
- MS
  - Known volumes of gas injected to establish a calibration curve for MS signal
  - Establishes an analytical technique that can quantitate hydrogen over time despite irregular peaks and simultaneous release of other species.



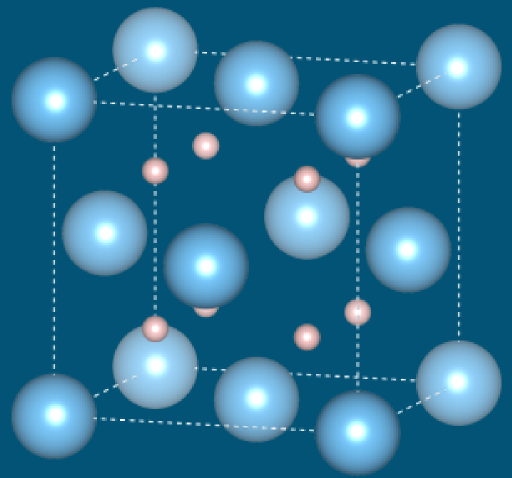
Standards would be useful but careful calibration and correction provide a path forward.

X-ray diffraction

- In δ-TiH_2 the Ti atoms sit on an FCC lattice with the 8 tetrahedral sites occupied with hydrogen
- Random, fractional occupancy of interstitial sites in sub-stoichiometric δ-TiH_x
  - Lattice parameter proportional to hydrogen occupancy
- δ-TiH_x is stable down to $x \approx 1.54$
  - α-Ti or β-Ti nucleates at lower concentrations
  - A second phase shows up as different peaks
- Phase quantitation possible via Rietveld refinement



Quick analysis and includes phase information.



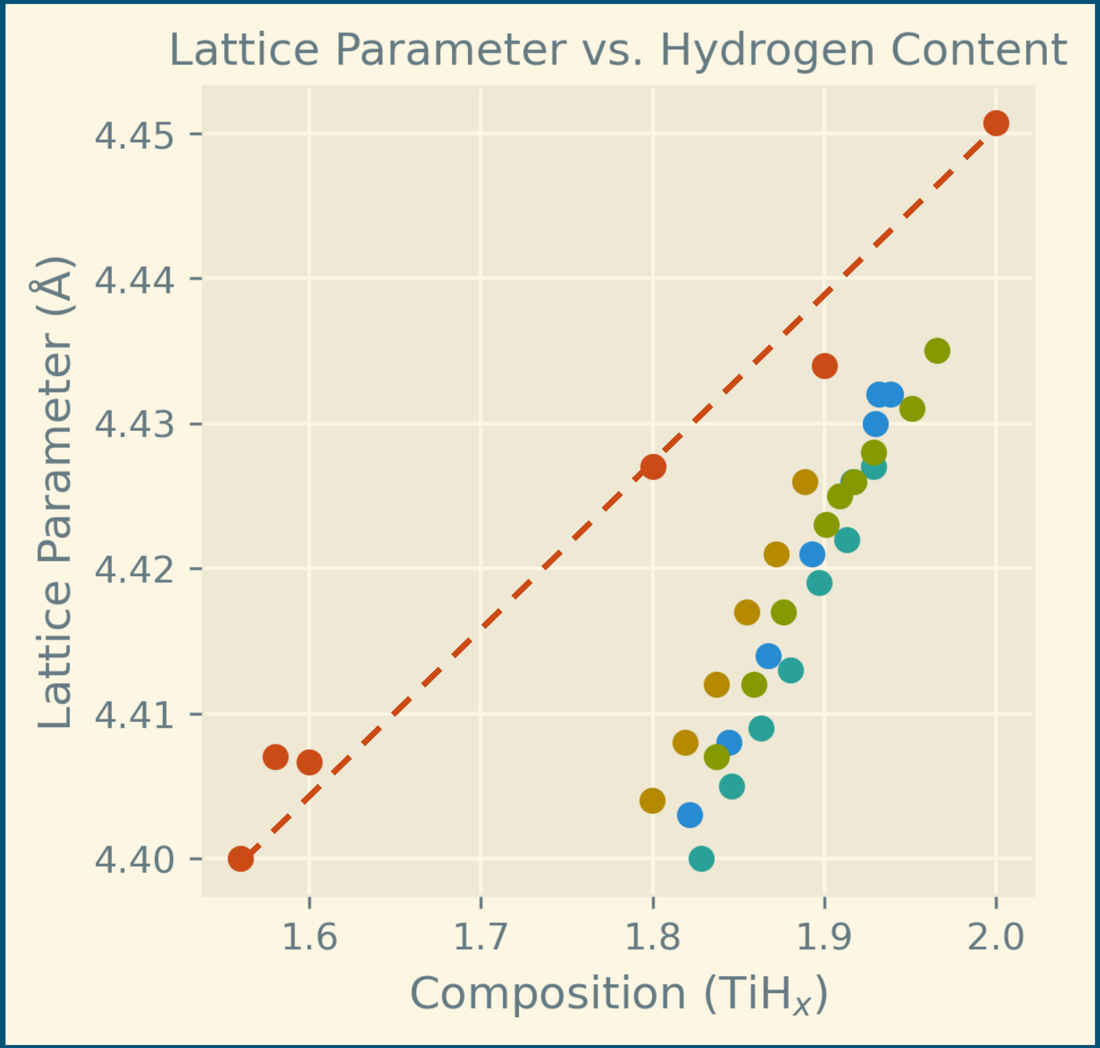
δ-TiH_2 Unit cell rendered in VESTA

Nominal composition	Calculated composition
1.45	n/a
1.55	1.56
1.65	1.58
1.75	1.76
2.00	1.96

X-ray diffraction

- XRD studies of TiH_x go back decades
  - However, some (especially older) samples are of questionable purity
  - Shows a definite linear relationship
  - Can be overcome by establishing a few standard hydrogen compositions and creating a calibrated database.

- Concerns
  - Other factors may cause peak shifts
    - Material: presence of impurities and strain
    - Instrument: Z-Height, optic misalignment, thermal expansion



Still reliant on computed or measured reference and signal not unique to hydrogen.

Summary

- Precision quantification of hydrogen in hydrogen-rich TiH_x remains challenging
- Composition may include multiple phases of varying hydrogen content
  - Important to consider total hydrogen content and phase fractions
- Explored several techniques that can provide complementary information
- Need for high-hydrogen standards (0.1 to several wt. % hydrogen)

Acknowledgements: Andre Benally, Shaun Hightower, Benjamin Juba, Jessica Kustas, Melody Teixeira, Michael Thomas, and Hua Wang