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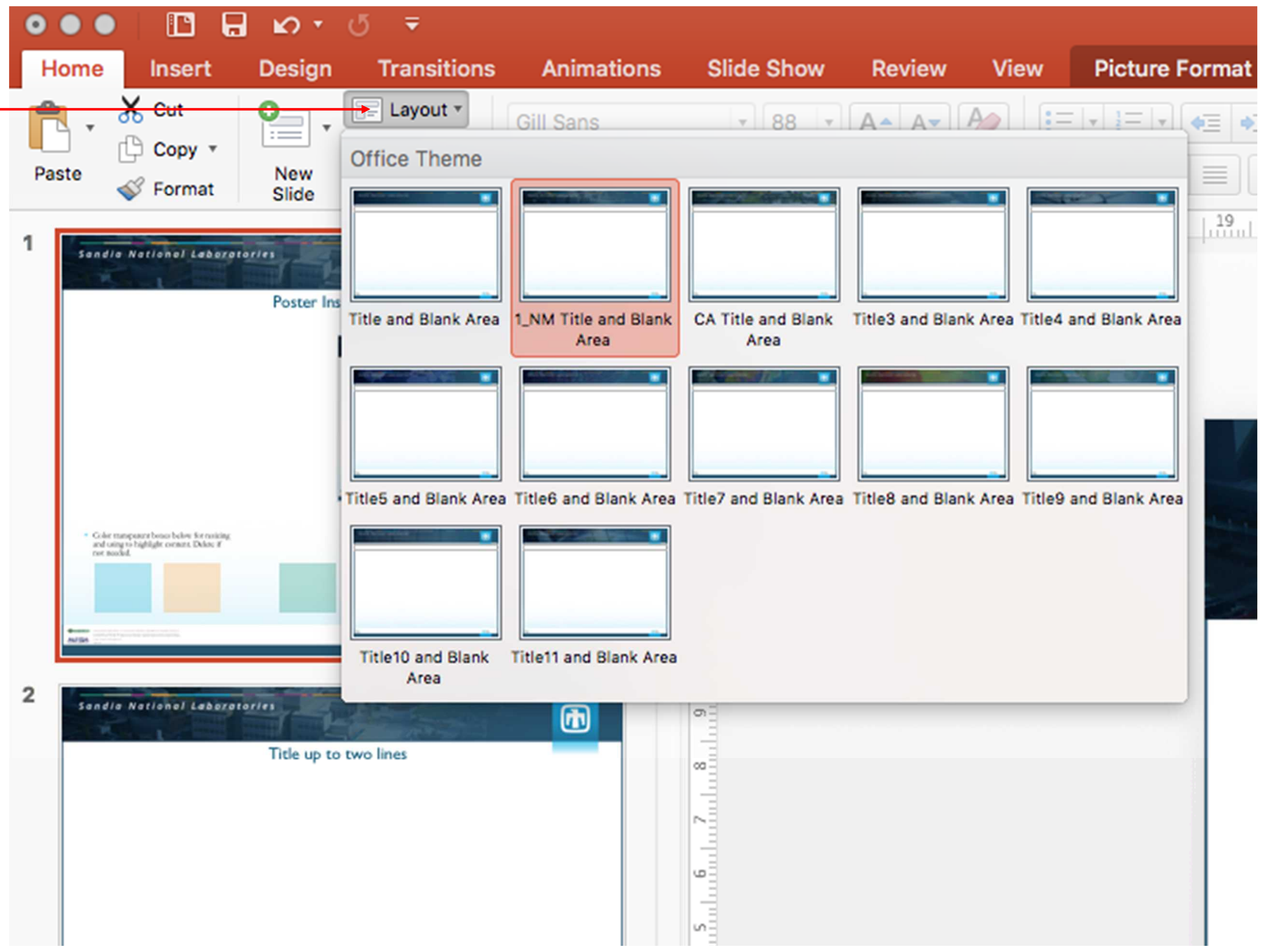

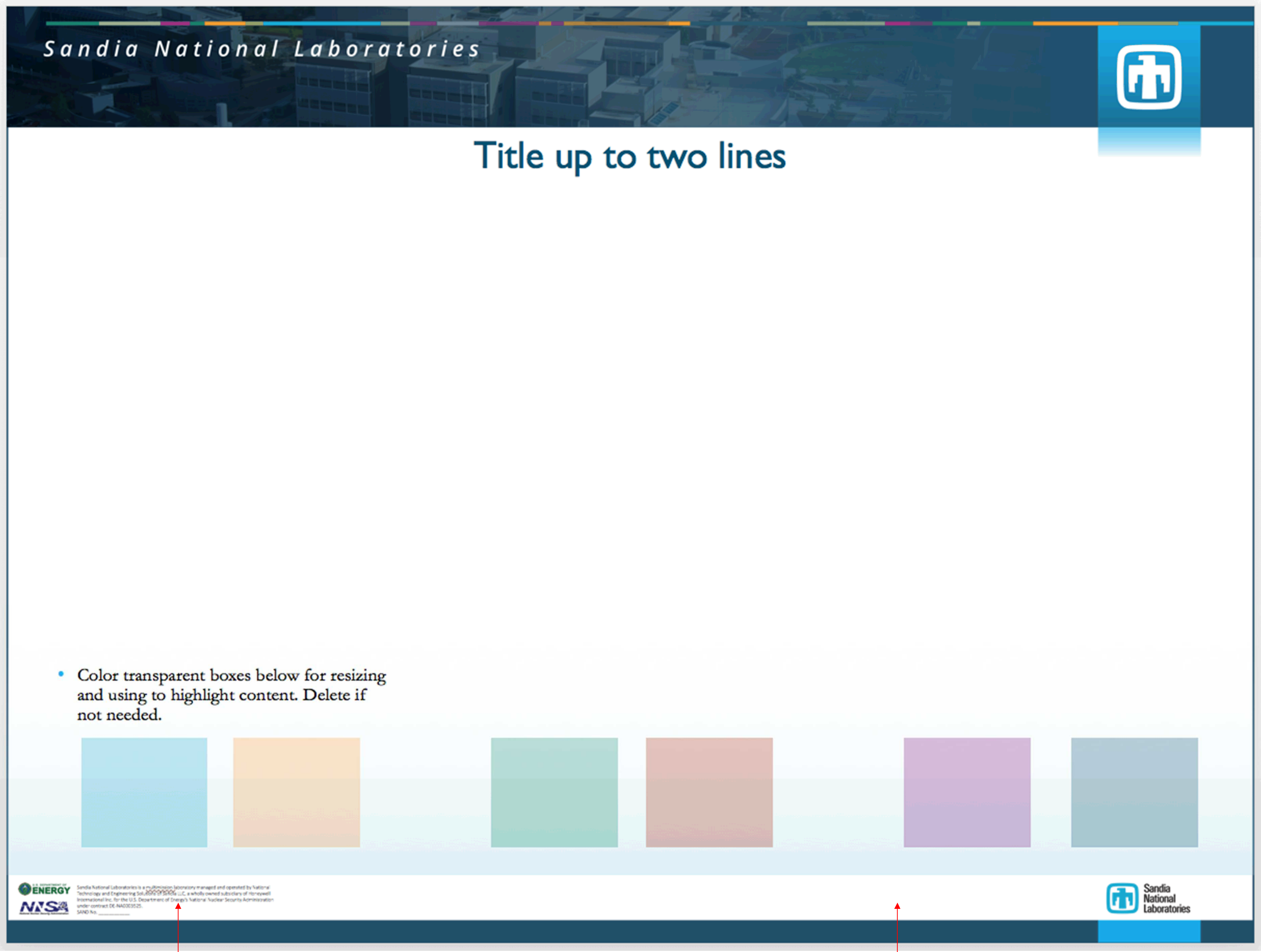

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Title up to two lines

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Determining Activation Temperatures in Group III & IV Metals via XPS

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Motivation

Rare-earth and transition metals are often used in hydrogen storage applications. However, these metals tend to passivate when exposed to air, which reduces their ability to sequester hydrogen during processing. In industry, high temperature is used prior to loading to breakdown the native oxide layer and therefore thermally "activate" the metal. The aim of this study is to determine the approximate minimum temperature by which a given metal can be considered thermally activated. *In-situ* XPS of Group III and IV metals during thermal annealing was performed to determine the phase content of the sample surface as a function of temperature.

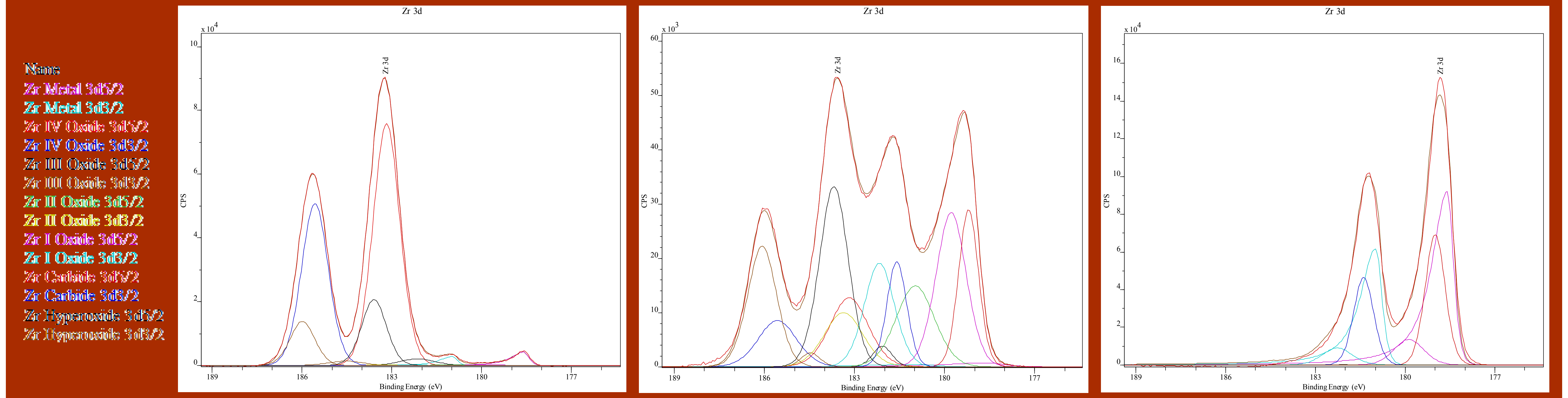
Experimental Methods

- **Samples were synthesized via electron beam evaporation under UHV conditions and from high purity precursor metals**
- **Samples were exposed to lab air for a period of several weeks to allow for native oxide layer formation**
- **Samples were then heated in increments of 100 °C (up to 900 °C), with a one hour wait period between spectrum collections**
- **CasaXPS software was used to analyze the resulting spectra**

XPS Fitting Methods

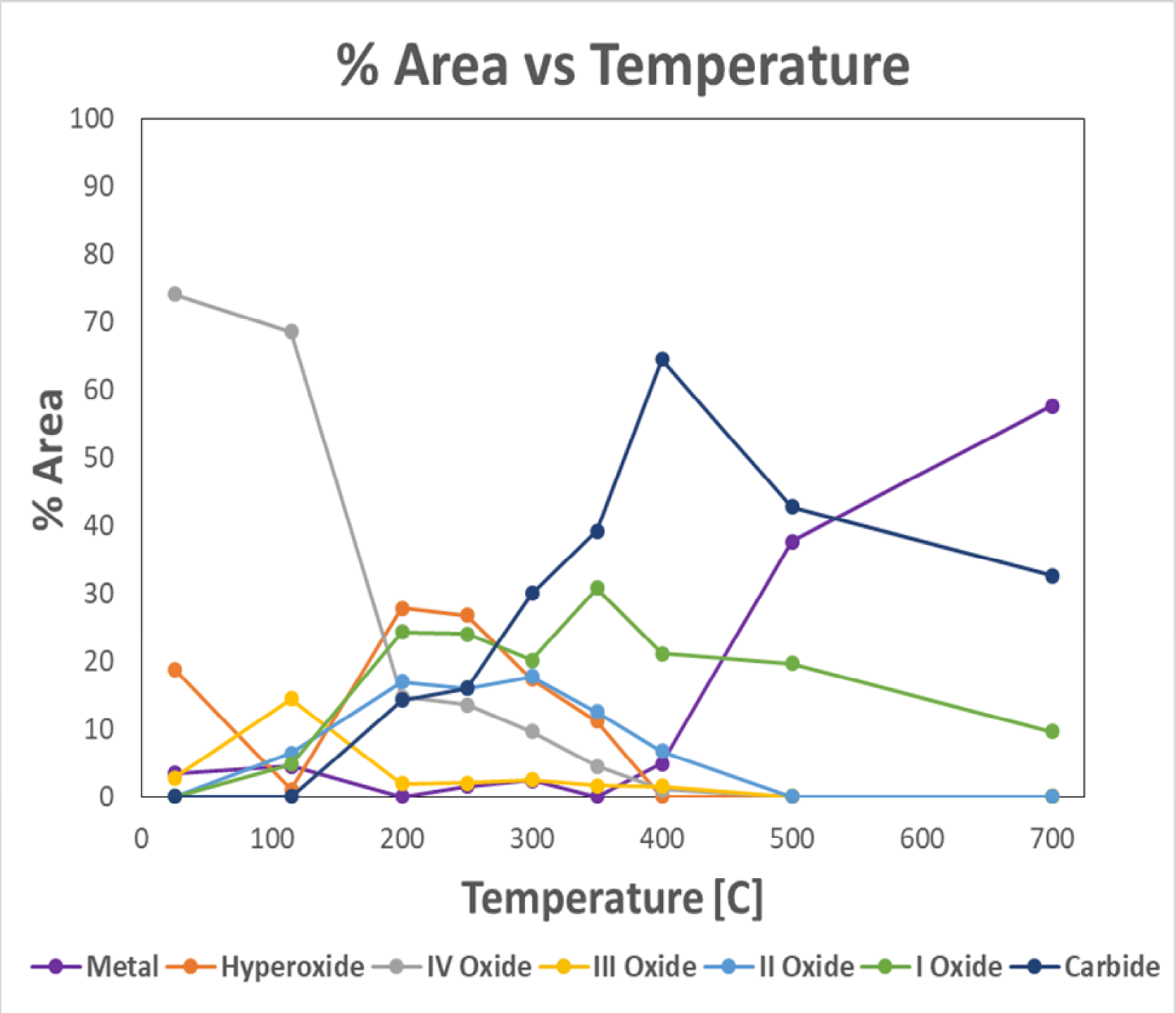
- **Metal peaks were fitted to an asymmetrical peak shape of the form LA(1.1,5,7)**
- **FWHM values between doublet peaks were constrained to be equal for Zr and Y**
- **FWHM values in Sc and Ti were only constrained with maximum values due to Coster-Kronig broadening**
- **Peak positions were constrained to within one standard deviation of the average value based on the NIST XPS database, then constrained to +/- 0.05eV when propagating the resulting fit**

Results

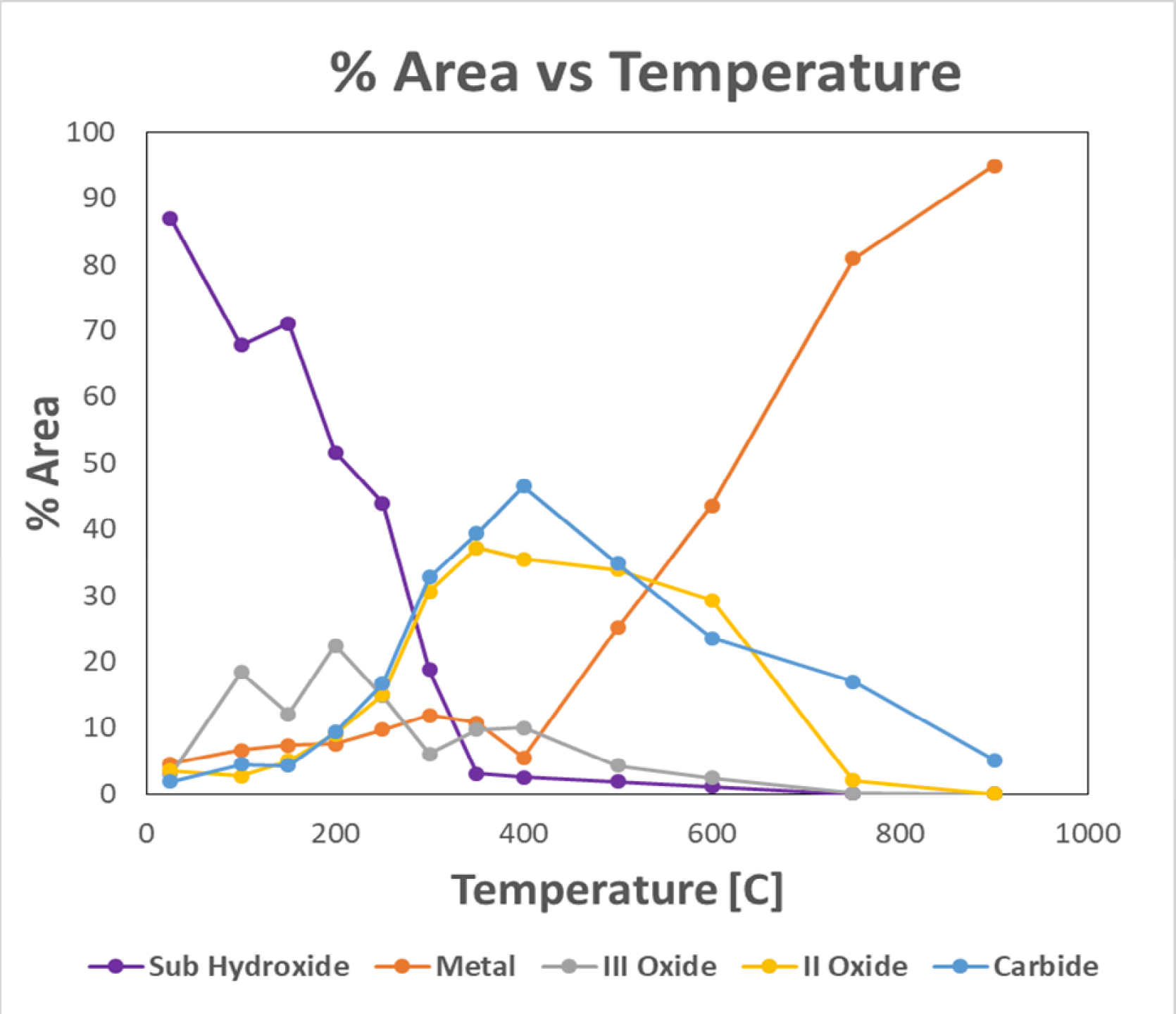


Ground State (23 °C) Transition State (250 °C) Activated State (700 °C)

For Zr, the activation temperature was found to be between 500-700 °C, when the Zr 0 2p 3/2 peak becomes the peak with the highest intensity and largest area. Metastable sub- and hyper- oxides as well as a carbon deficient carbide phase were seen to form during the annealing process. Similar behavior was seen in the other metals studied, though Sc and Y showed evidence of hydrous species whereas Zr and Ti did not.



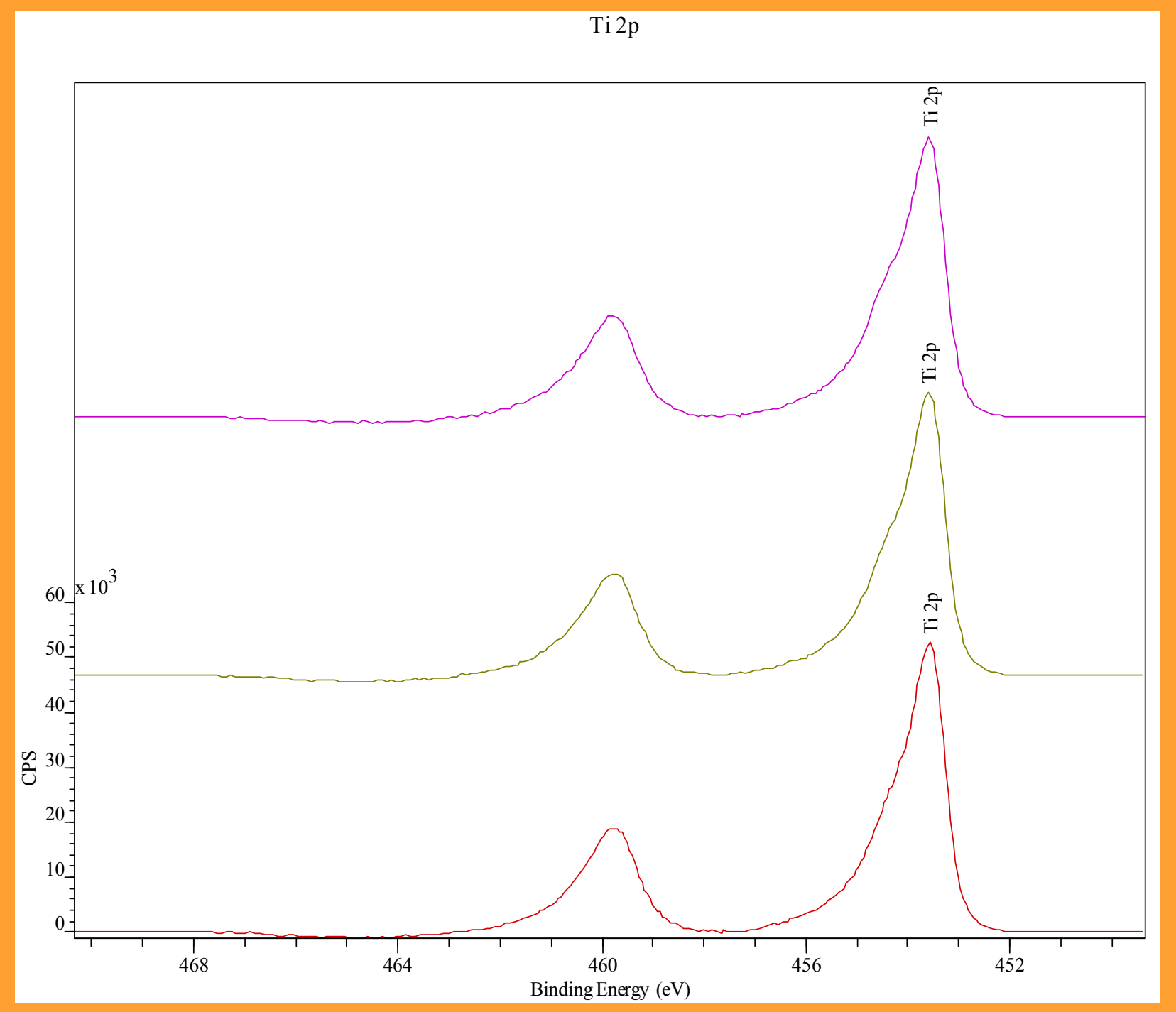
Zr Activation Process



Sc Activation Process

Zr and Ti were found to undergo four distinct steps in the annealing process where Y appears to only undergo two. In all of the metals, mild temperatures serve to desorb surface contamination and to crystallize metastable hyper- and sub- oxides in their stable oxides. In Y, the stable hydroxide species simply diffuses into the bulk, leaving behind the metal and doing so at relatively low temperature. In Zr and Ti, suboxides are formed first, followed by the growth of a carbon deficient carbide phase, and ending with the decomposition of the carbide phase into the bulk at high temperatures. Sc has a stable hydroxide phase at room temperature like Y does but appears to also form suboxides like Zr and Ti. Sc appears to also form a stable carbide phase as well.

Supplemental Results



Spectra were taken at the same temperature at 40 min intervals to show that the activation process was purely due to thermal energy and therefore not dependent on time at temperature or other kinetic factors.

Conclusions

- **Determined activation temperatures: 500-700 °C for Zr, 400-500 °C for Ti, 600-750 °C for Sc, and 200-300 °C for Y**
- **Relative stability of the suboxides and carbide phases seems to be a determining factor in the magnitude of the activation temperature**

References

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