

Monitoring of FeS₂ reactions using high temperature XRD coupled with Gas Chromatography (GC)

Kerry-Ann M. Stirrup, Mark A. Rodriguez, Eric N. Coker, James J. M. Griego, Travis M. Anderson

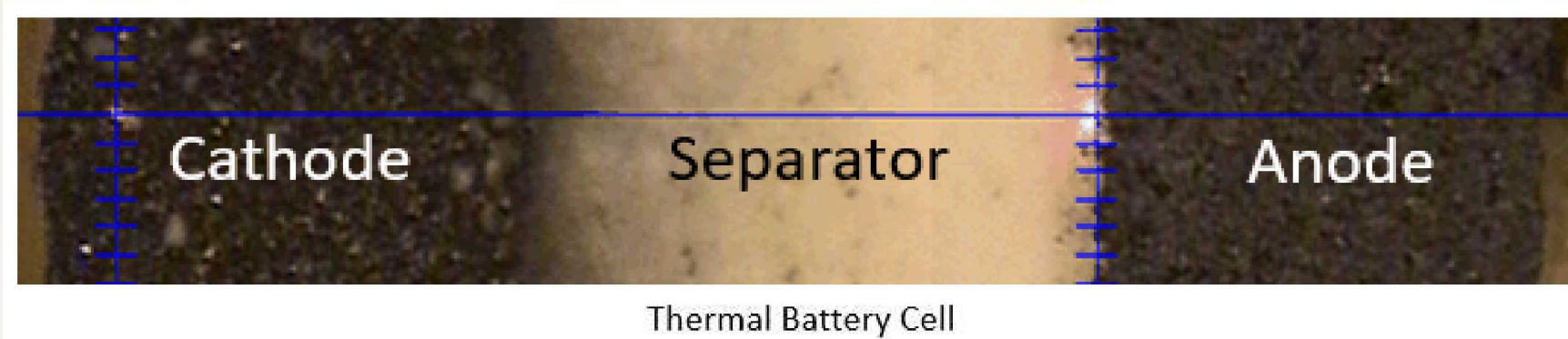
Sandia National Laboratories, Albuquerque, NM USA

Introduction

Thermally activated batteries require high levels of reliability, both in longevity and electrical stability. FeS₂ cathode materials are employed in thermal battery builds, and while aspects of empirical performance of their cathode materials have been evaluated during discharge, little is known about the scientific aspects of cathode behavior at temperature. We have investigated the thermal decomposition of the FeS₂ material under differing atmospheric conditions in the presence of LiCl and KCl electrolytes. Our approach is twofold:

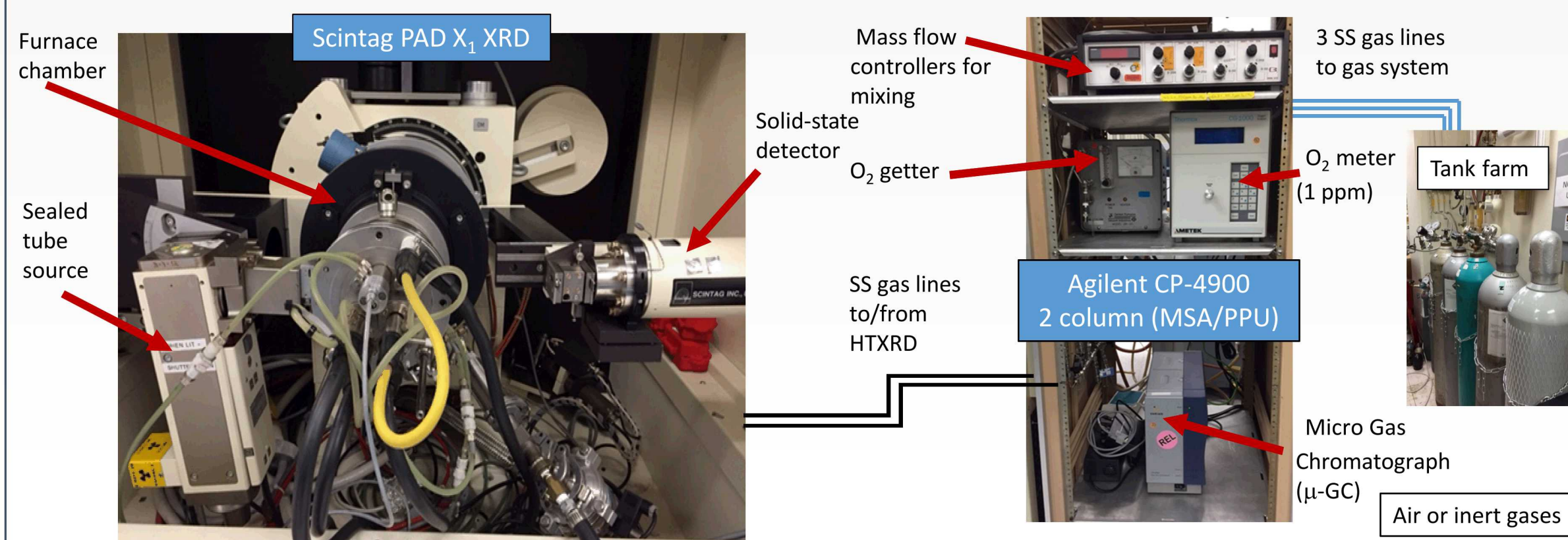
- In-situ High Temperature X-ray Diffraction (HTXRD) coupled with concurrent Gas Chromatography (GC)
- Analysis is augmented by Differential Scanning Calorimetry and Thermogravimetric Analysis (DSC/TGA) coupled with Mass Spectroscopy (MS)

Synergy of these multiple analysis techniques yields valuable insight into the FeS₂ reaction in air, as well as to the impact of thermal decomposition on the ultimate functionality of a fabricated thermal cell.



Experimental

1. High Temperature X-Ray Diffraction with Gas Chromatography



Powder samples were dispersed in a methanol solution, deposited onto an alumina substrate, and sealed into the furnace chamber.

XRD Parameters:

- Step size (2θ): 0.04°
- Scan range (2θ): 26° to 41°
- Dwell (s): 1.0

Temperature Parameters:

- Heat increments (°C): 10
- Ramp Rate (°C/min): 50
- Temperature Range (°C): 25 to 550

*Gas composition analysis via GC was continuous throughout the XRD run.

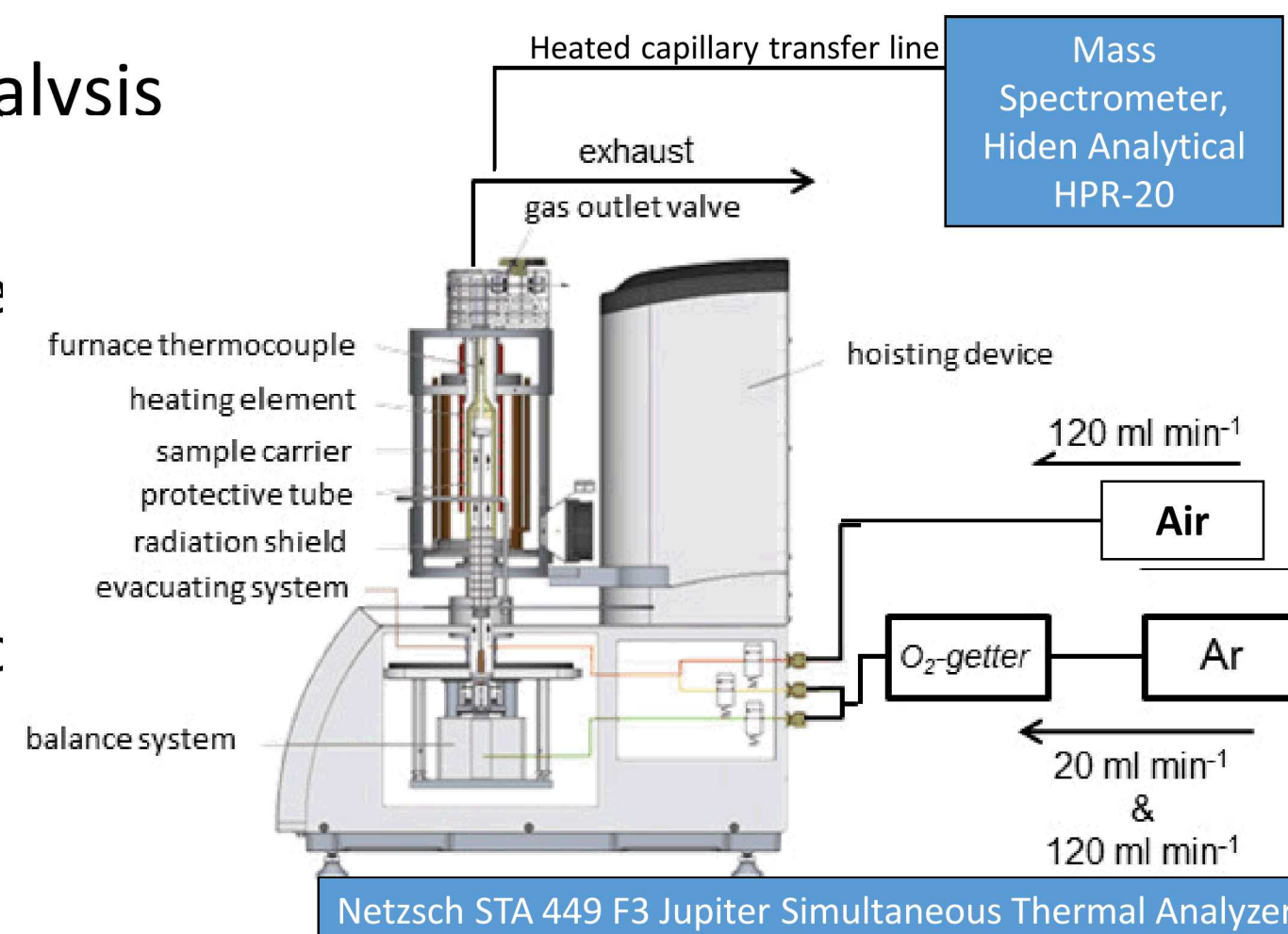
2. Simultaneous Thermal Analysis

Specimens were loaded into an cup and placed in the STA while minimizing air exposure.

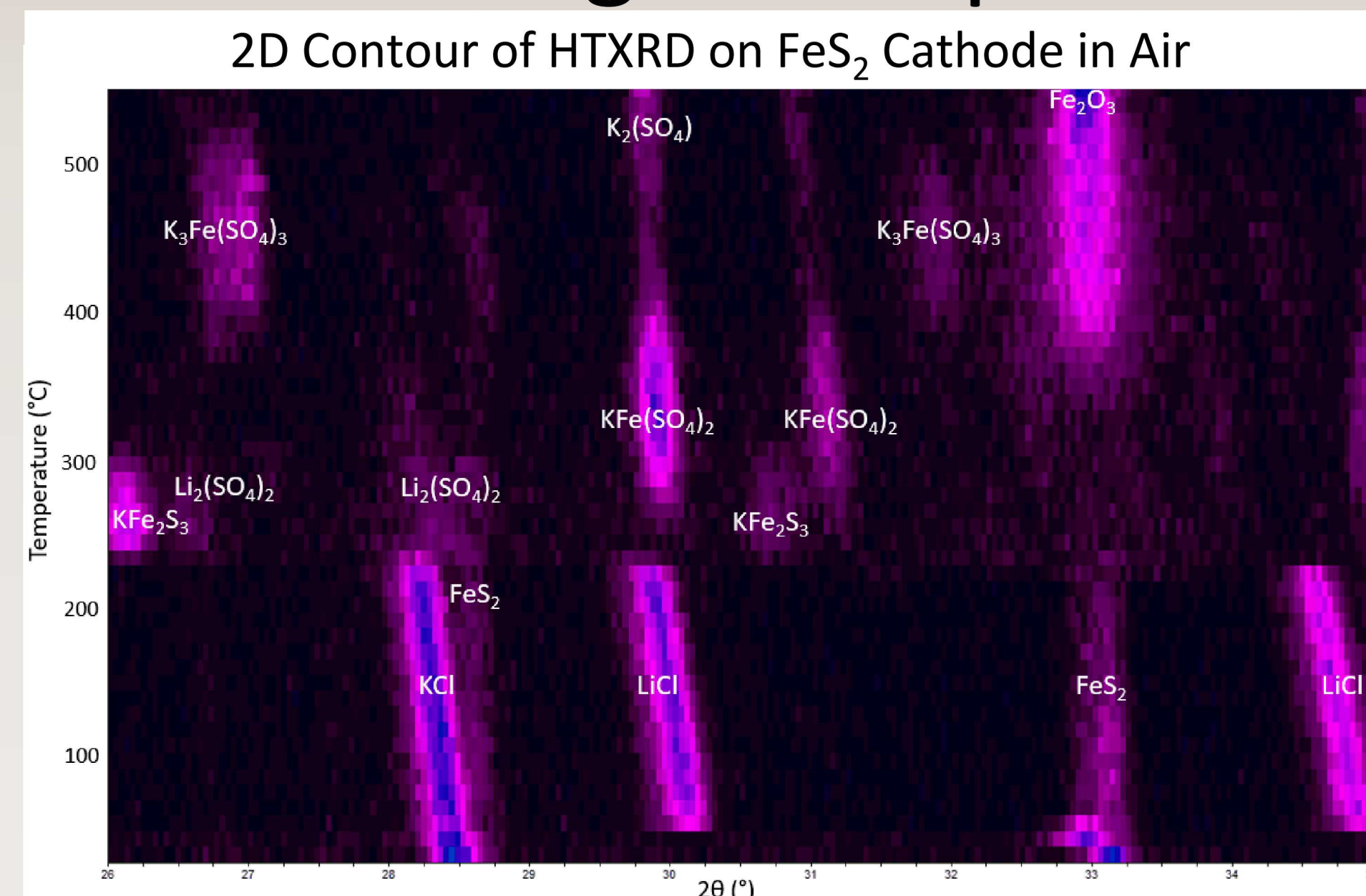
STA Parameters:

- Heating rate (°C/min): 5
- Temperature range (°C): 30 to 550

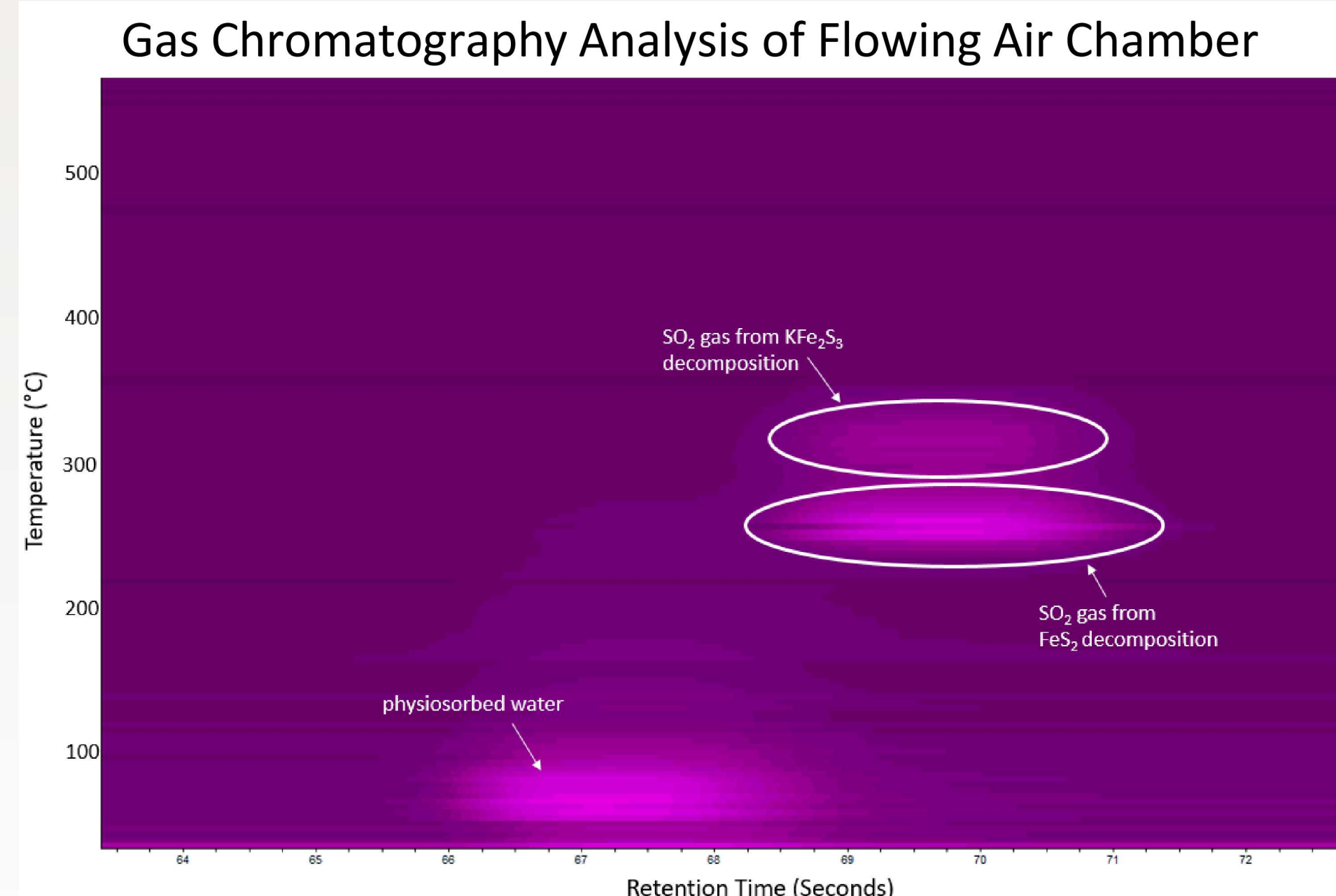
*Gas composition analysis via mass spectro was continuous throughout the STA run.



Oxidizing Atmosphere

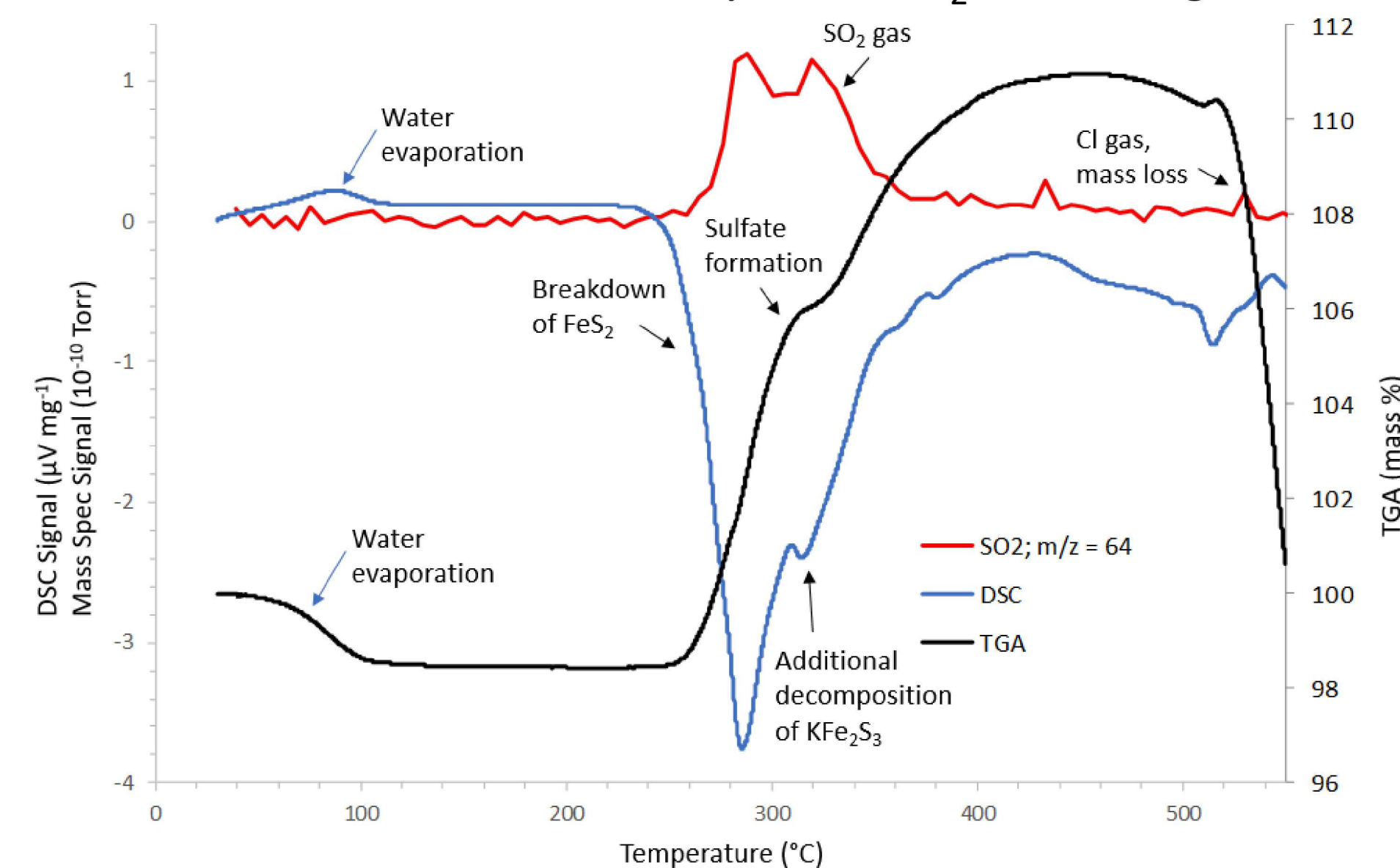


A significant chemical reaction with decomposing KCl and LiCl salt phases is observed at 240°C. Additional heating results in the formation and decomposition of intermediate sulfates, while Fe₂O₃ persists through 550°C.



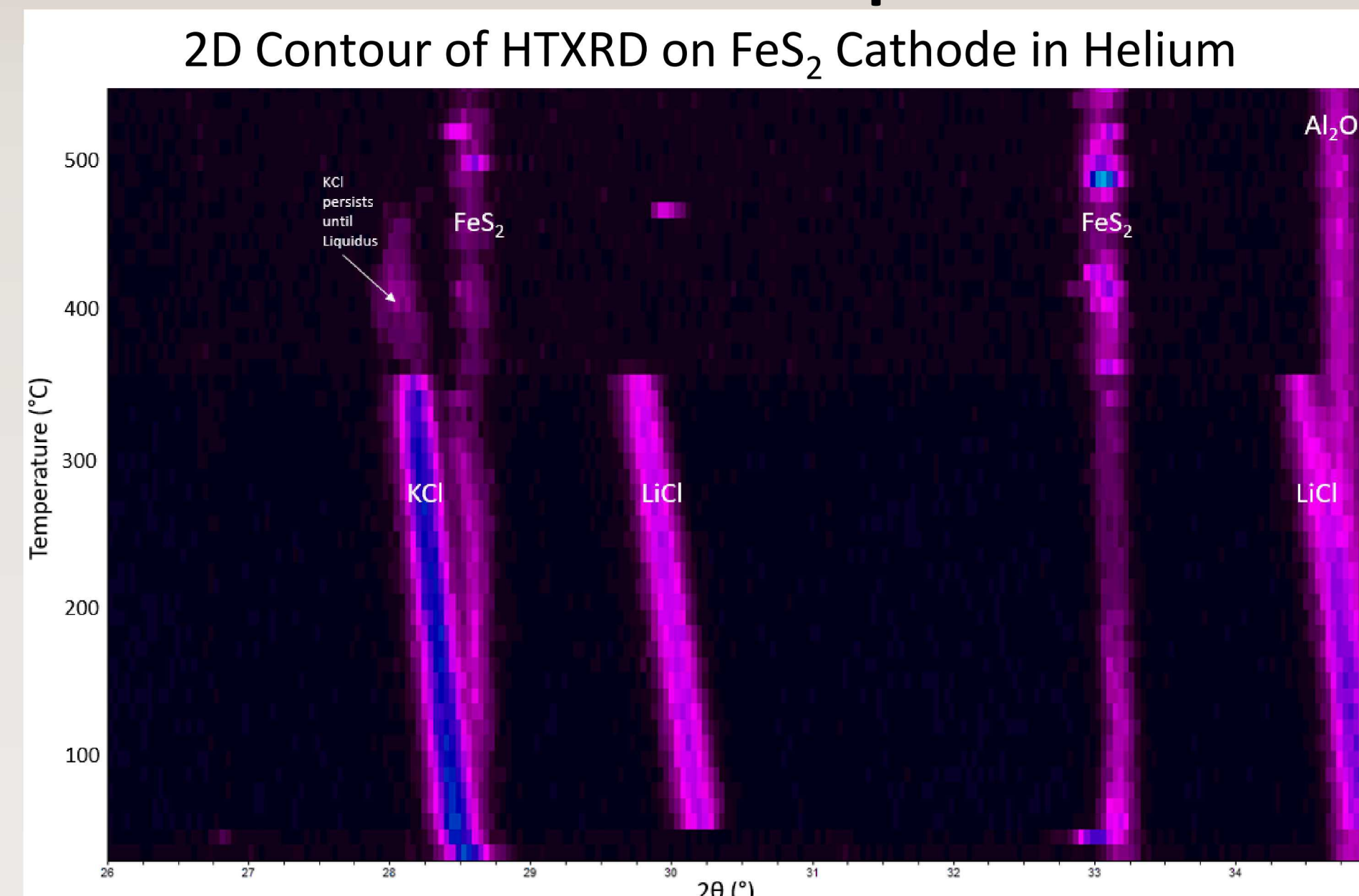
Concurrent GC measurements made on the gas output stream from the HTXRD reaction chamber detected the release of SO₂ gas in two distinct temperature ranges, confirming formation and decomposition of the sulfates during heating.

Simultaneous Thermal Analysis of FeS₂ in Flowing Air

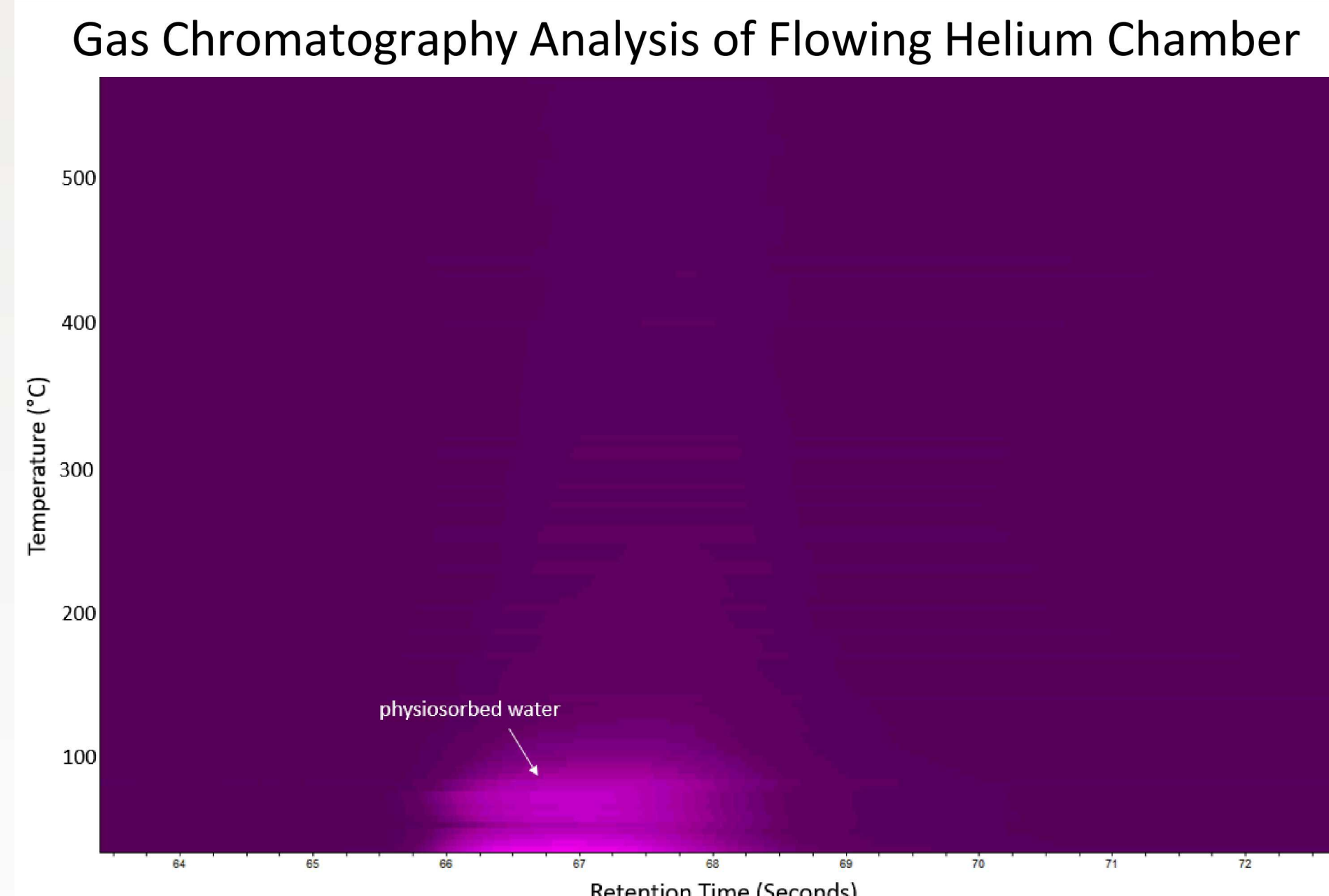


Independent thermal analysis of the cathode showed consistent thermal response to observed reactions in the HTXRD data. Most notable is the exothermic reaction of the salt phase at 280°C to form additional intermediate sulfates. MS detected two distinct SO₂ gas output, coincident with the decomposition of FeS₂ and KFe₂S₃.

Inert Atmosphere

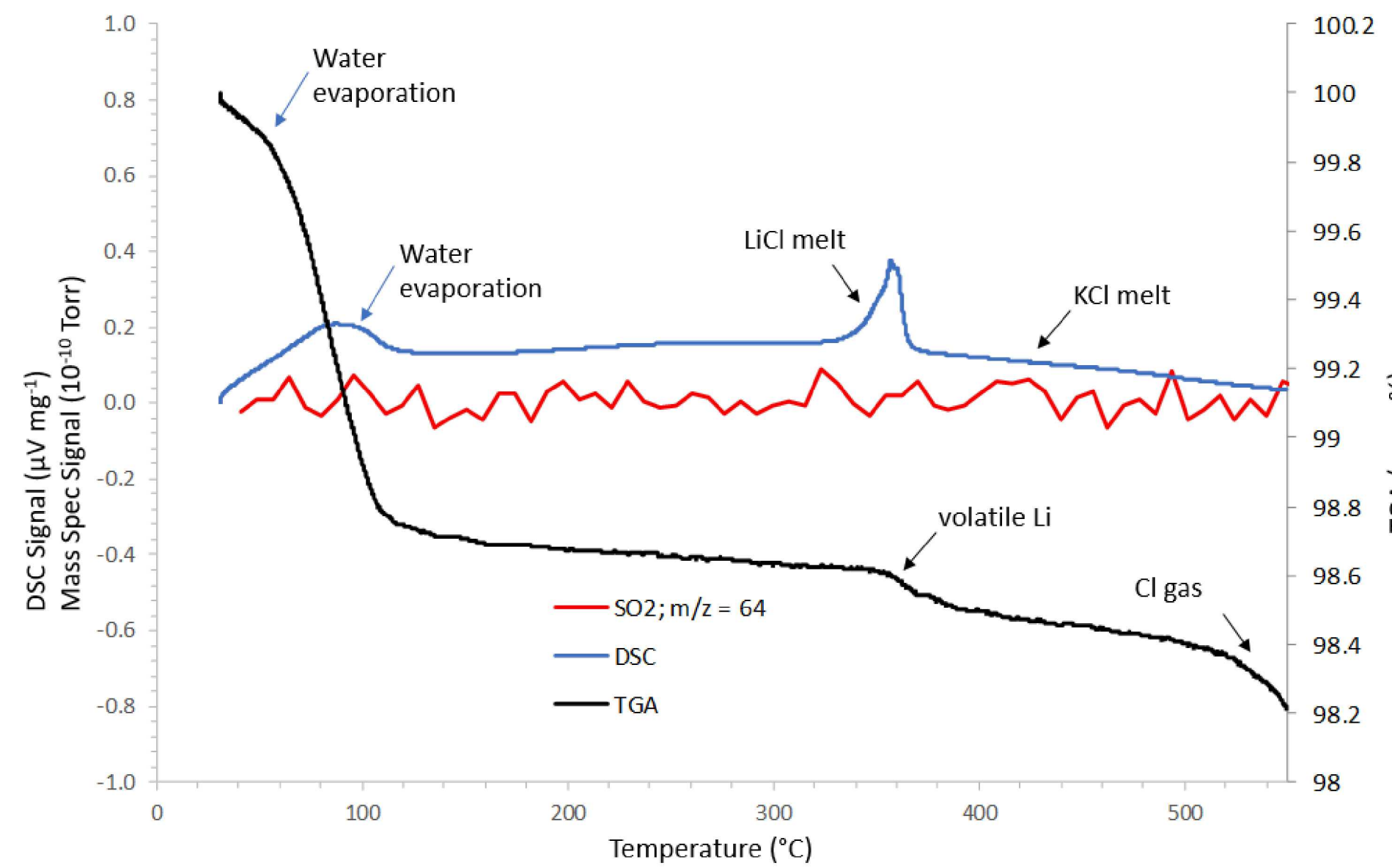


Heating the FeS₂ cathode in a Helium atmosphere shows little change to the pyrite phase. Characteristically, LiCl melts at 350°C while the full melt of KCl is delayed until 450°C. No additional phase transitions are observed.



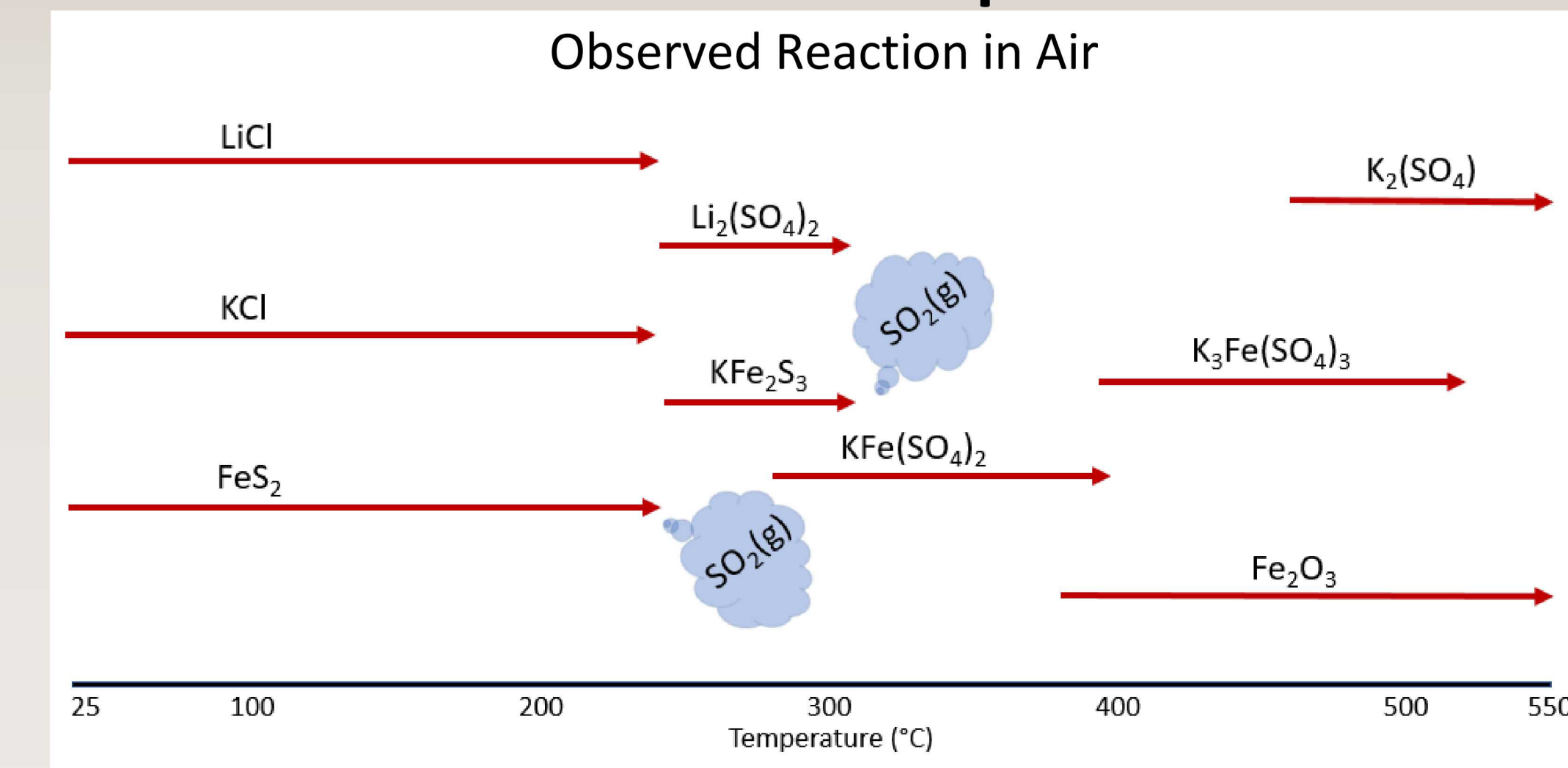
Concurrent GC measurements made on the output gas stream from the HTXRD reaction chamber detected no release of SO₂ gas, only the release of physisorbed water at low temperatures.

Simultaneous Thermal Analysis of FeS₂ in Flowing Helium



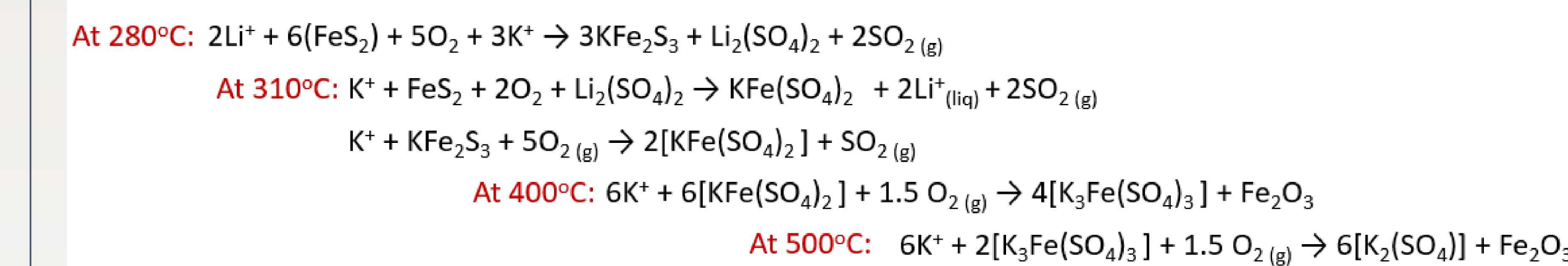
Additional independent thermal analysis of the cathode in inert conditions reveals a true melting endotherm for the LiCl phase at 350°C, with no significant release of SO₂ detected in MS analysis. This result is consistent with GC measurements. Cl gas released at 500°C is freed from the electrolyte melt but is not indicative of an additional reaction.

Reaction Sequence

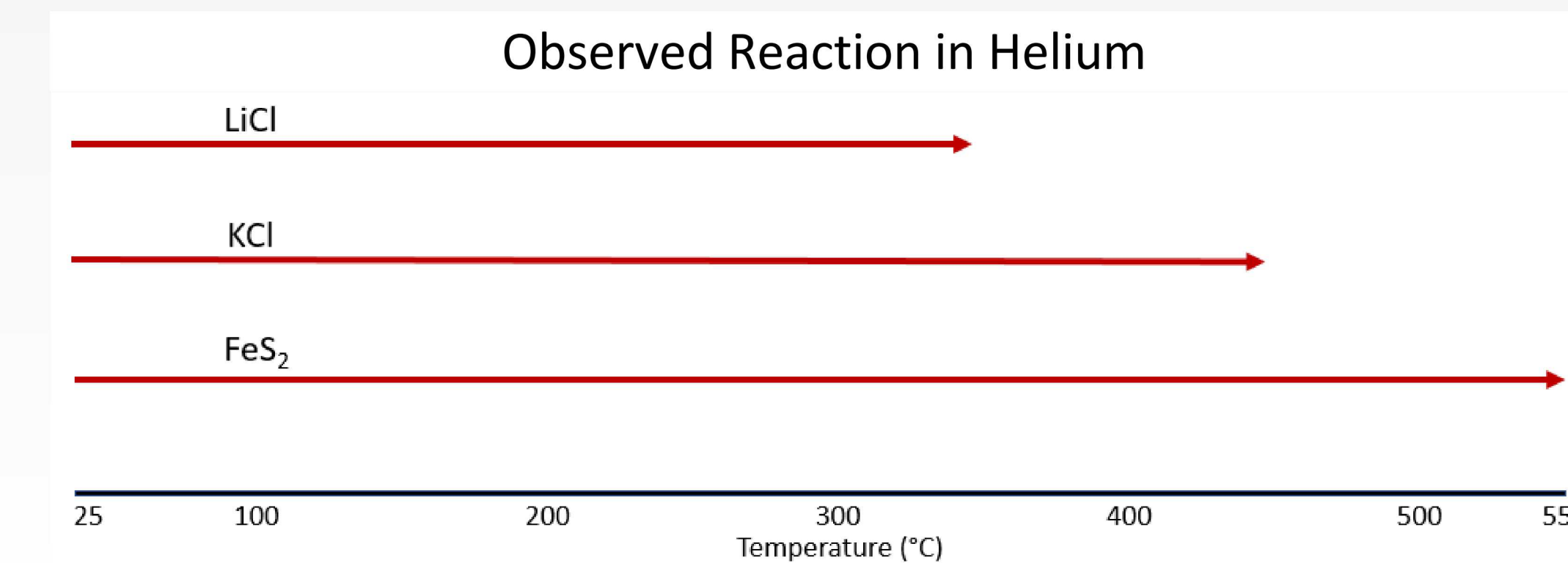


Notably, the final Fe₂O₃ phase formed has a cubic crystal structure similar to Yttria-stabilized Zirconia (YSZ) in the Ia-3 space group, and is not common rhombohedral Hematite. The Ia-3 defect Fe₂O₃ structure observed may have a proclivity for substitution, possibly incorporating available Li and K cations.

Cathode Decomposition Chemistry



The decomposition of initial KCl and LiCl salts at 240°C in the presence of an oxidizing agent triggers the onset of an irreversible chain reaction, resulting in the formation of the undesired compounds KFe₂S₃ and Li₂(SO₄)₂ which are not observed when heating in an inert atmosphere.



Here, KCl and LiCl dissipate into a liquidus phase indiscernible in XRD intensity.

Summary

- Under an air atmosphere, FeS₂ experiences an irreversible degradation at 280°C due to oxygen exposure resulting in impeded thermal battery performance
- Cathode degradation is characterized by generation of KFe₂S₃, Li₂(SO₄)₂, and KFe(SO₄)₂ which cause a significant exothermic reaction and release of SO₂ gas during decomposition
- Independent thermal analysis experiments augment the in-situ XRD results and support the overall picture of FeS₂ decomposition
- Under an inert atmosphere, FeS₂ experiences no significant reaction and generates no gaseous output
- Detection of SO₂ gas presence provides a non-destructive criteria for determination of cathode viability
- ❖ Possible future work: Determining what percentage of oxygen exposure is detrimental to the cathode material