

Methods

Isoperibol Calorimetry

Surroundings at constant temperature, change in temperature of sample causes heat flow which is measured.

High temperature oxide melt solution calorimetry

Typically used solvents:
At 700-800 °C: Sodium Molybdate $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$
Lead Borate $2\text{PbO}\cdot 2\text{B}_2\text{O}_3$
Alkali Borate $\text{LiBO}_2\cdot \text{NaBO}_2$

Solution experiments

Sample equilibrated at calorimeter temperature, then dissolved in the oxide melt.

Measured quantity: Enthalpy of solution (H_s at calorimeter temperature.

Used for: Enthalpy of formation at calorimeter temperature. Mixing enthalpy at calorimeter temperature. Enthalpy of phase transitions.

Drop solution experiments

Sample dropped into solvent from ambient temperature.

Measured quantity: Enthalpy of drop solution (H_{ds} from room temperature into solvent at calorimeter temperature.

Used for: Enthalpy of formation at 25 °C. Mixing enthalpy at 25 °C. Enthalpy of phase transitions., etc.

For samples which do not persist at calorimeter temperature. For samples which evolve gases. Routinely used for many other samples.

Transposed temperature drop experiments

Sample dropped from ambient temperature into empty calorimeter.

Measured quantity: Enthalpy of transposed temperature drop (H_{td}).

Used for: Heat content
Enthalpy of phase transitions
Enthalpy of devitrification
Enthalpy of dehydration
Enthalpy of oxidation.

Differential Scanning Calorimetry (DSC)

Sample is heated or cooled at a given rate and heat flow is monitored compared with reference.

Measured quantity: Differential heat flow.

Used for: Specific heat
Enthalpy of phase transition
Enthalpy of reaction.

DSC measurements capable of yielding quantitative enthalpy data, apart from classical differential thermal analyses (DTA).

DSC and DTA methods benefit combined with Thermogravimetry (TG) and Evolved Gas Analyses (EGA), - sample weight change during heating measured with microbalances and presence and composition of the evolved gas monitored by means Mass Spectrometry (MS) or Fourier Transform Infrared spectrometry (FTIR).

Why I Count Calories for a Living

They are fascinating. Energetics whispers secrets of the strength of chemical bonds. Entropies sing of vibrating atoms, moving electrons, and structural disorder. Systematics have predictive power.

They pay. Thermodynamic data are essential to good materials processing and materials compatibility. Environmental science needs thermodynamics, both for issues of stability and as a starting point for kinetics. Mineralogy, petrology, and deep Earth geophysics need thermodynamic data.

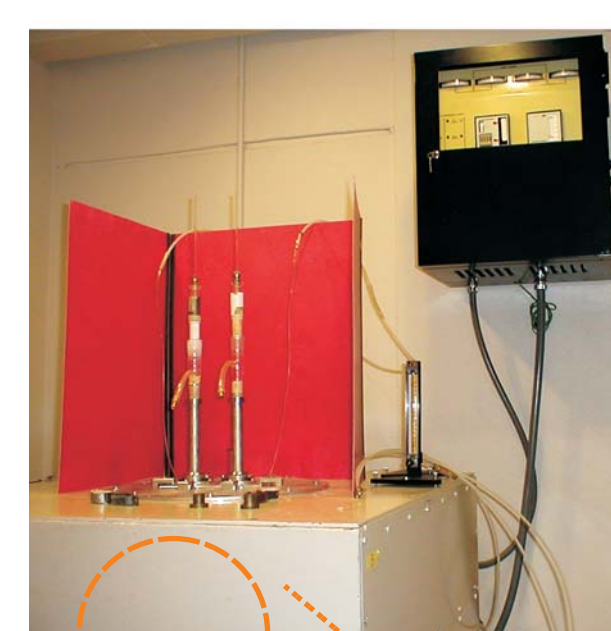
Alexandra Navrotsky

Equipment

Tian-Calvet type calorimeters

Heat flow generated by reaction is measured by thermopile surrounding sample.

Custom built high temperature isoperibol twinned microcalorimeters

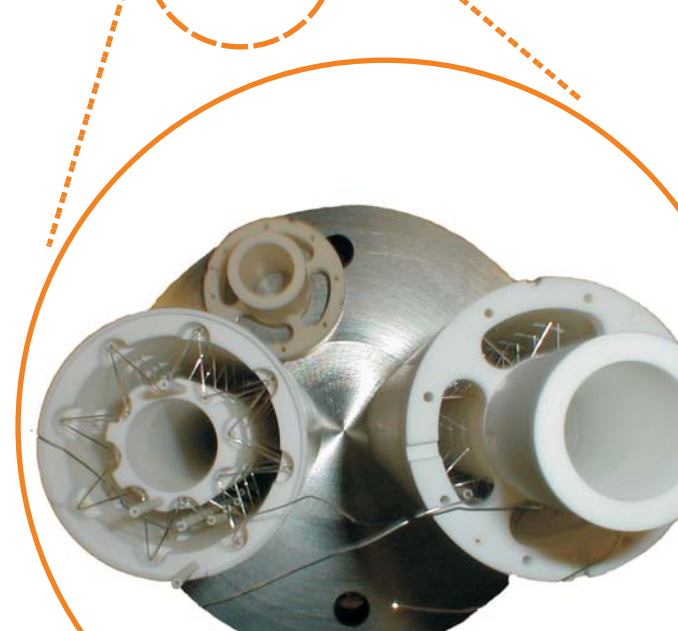


"Regular" microcalorimeter operated at 700 or 800 °C (shown on the photo and schematic), allow for measurements on 5 mg samples to be done routinely.

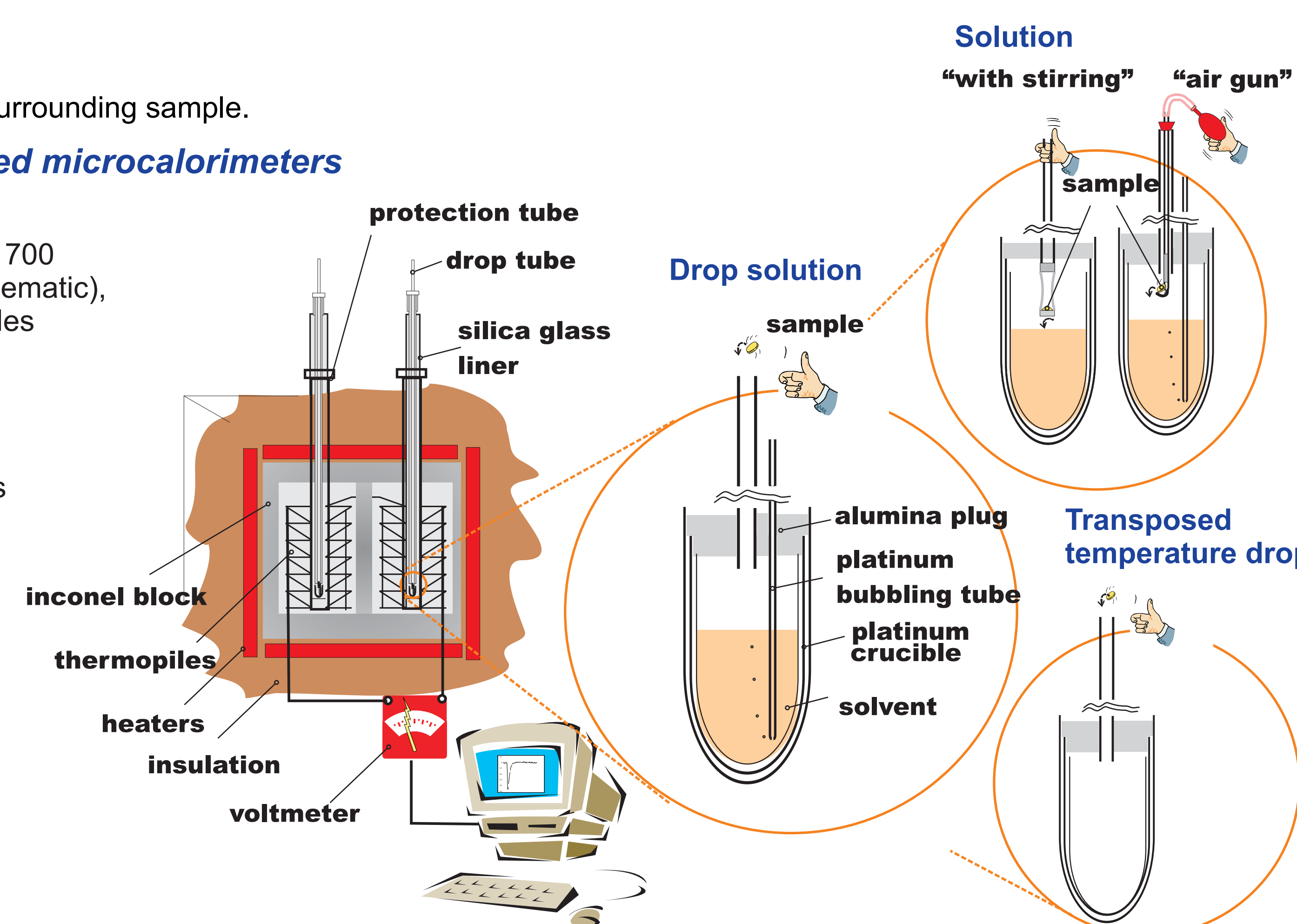
"Ultrasensitive" microcalorimeter (not shown) operated up to 900 °C allows measurements on 1 mg samples to be done routinely.

Room temperature is controlled at 25 ± 0.5 °C and humidity at $50 \pm 5\%$, attainable accuracy of calorimetric experiments is ± 1 to $\pm 2\%$.

The accuracy of heats of formation obtained is typically ± 1 to ± 5 kJ/mol.



Thermopiles with inconel block removed, as viewed from the top



Commercial Tian-Calvet type calorimeters

C80 BT215



Setaram **C80** and **BT215** are Calvet-type twin microcalorimeters. Temperature range: **C80**: 25 to 300 °C, **BT215**: -196 to 200 °C.

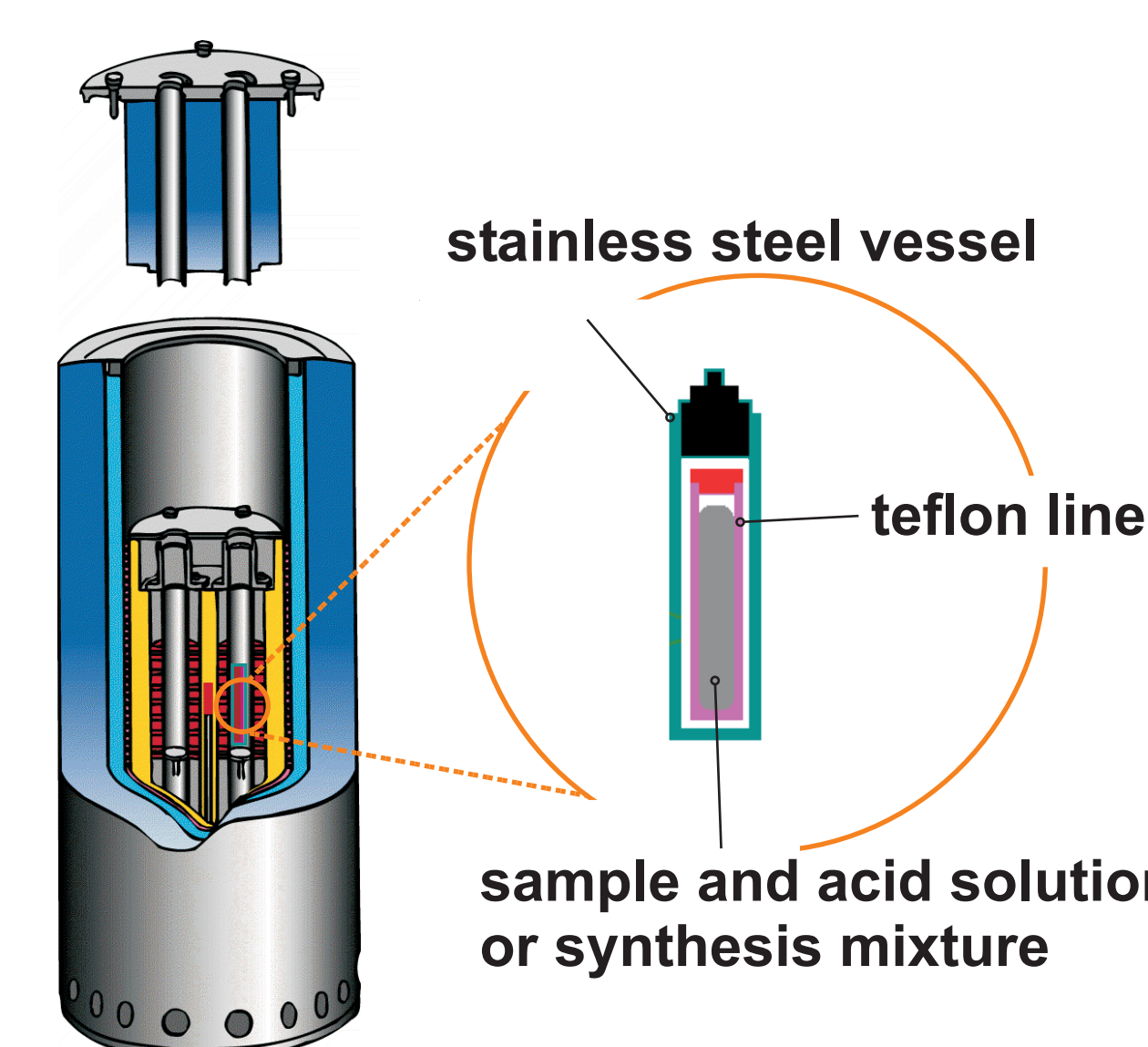
They can be operated either isothermally (initial stabilization ~ 2 hrs with temperature fluctuation within 0.01 C) or in scanning mode (0.001 to 2.0 °C/min). Used for in-situ synthesis calorimetry (cell size available for sample, 7.5 g), HCl and HF solution calorimetry (solid sample size, 2-50 mg vs. solvent size 5 g).

MHTC-96 HT1500



MHTC-96 equipped with graphite furnace and operational from room temperature (RT) to 1500 °C. It can be used with TTD setup isothermally or in scanning mode with heating rate of up to 10 °C/min, with DSC sensor or with thermobalance (shown on the picture) at a heating rate up to 5 °C/min.

Its predecessor, **HT1500** is mostly used with drop solution setup at 1100-1400 °C using silicate melts as solvents for calorimetry.



C80 and BT215 with setup for acid solution or reaction calorimetry

Commercial differential thermal analyzers (DTA) and scanning calorimeters (DSC)

Netzsch 400 series - Heat flow DSC and DSC/TG high-temperature apparatus

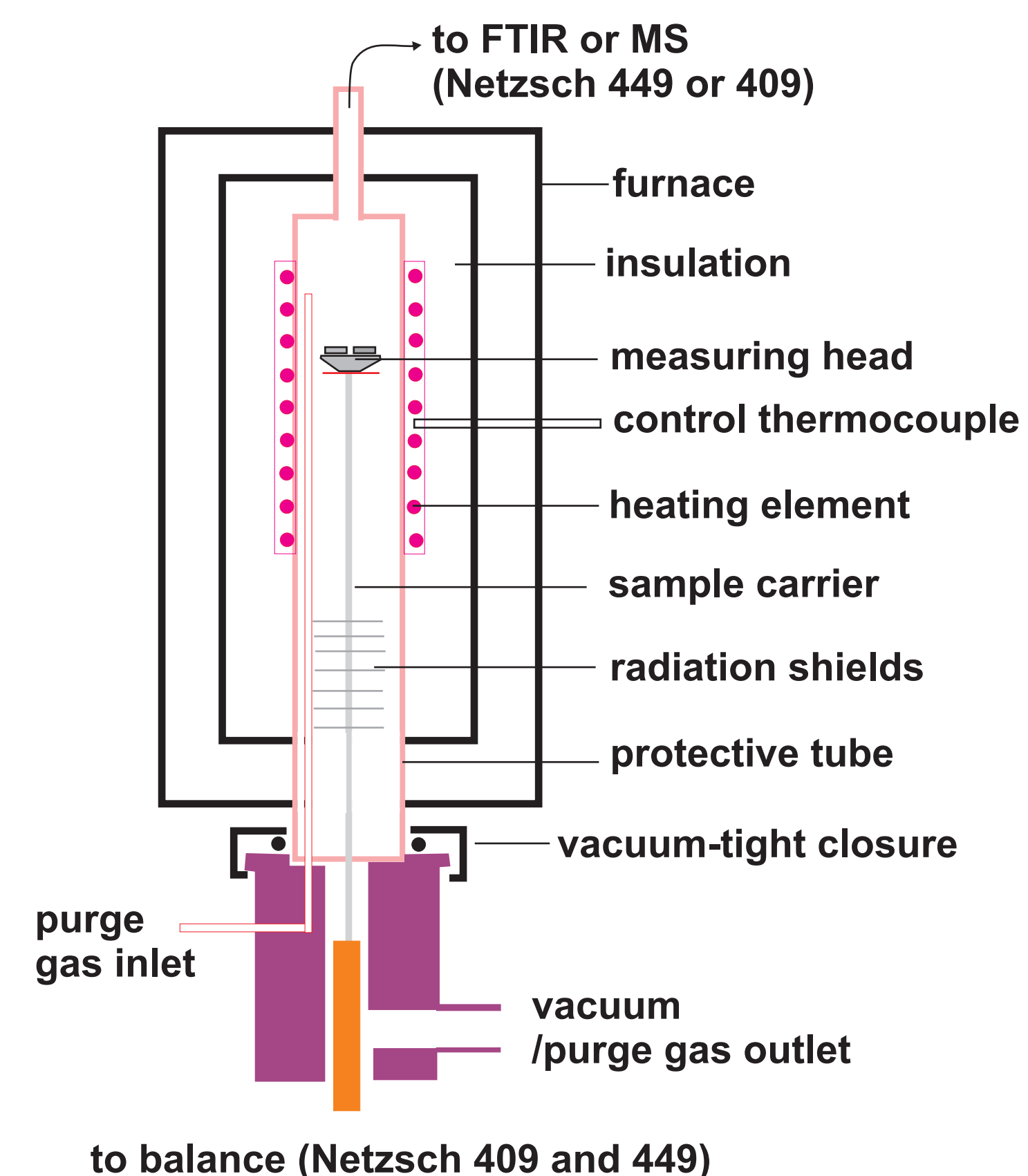
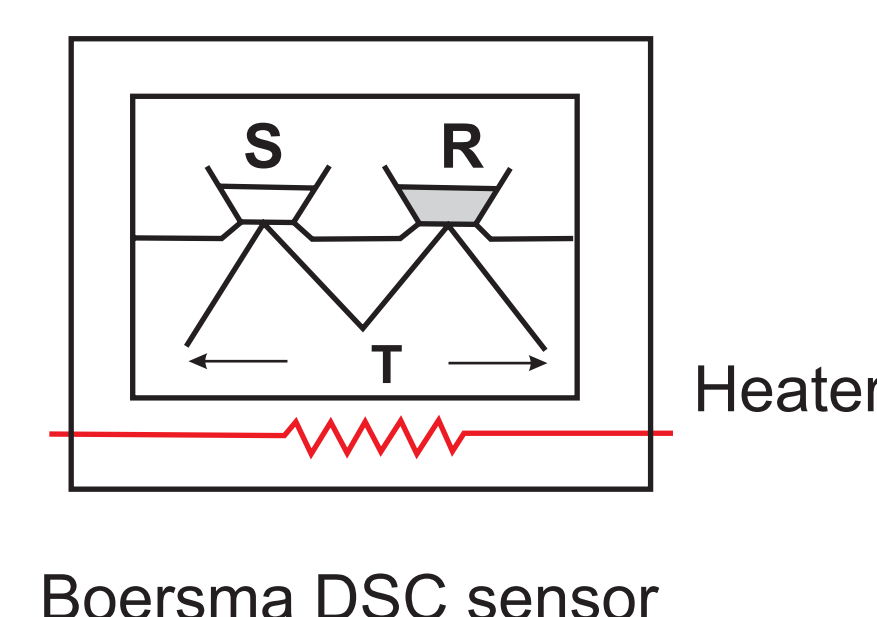
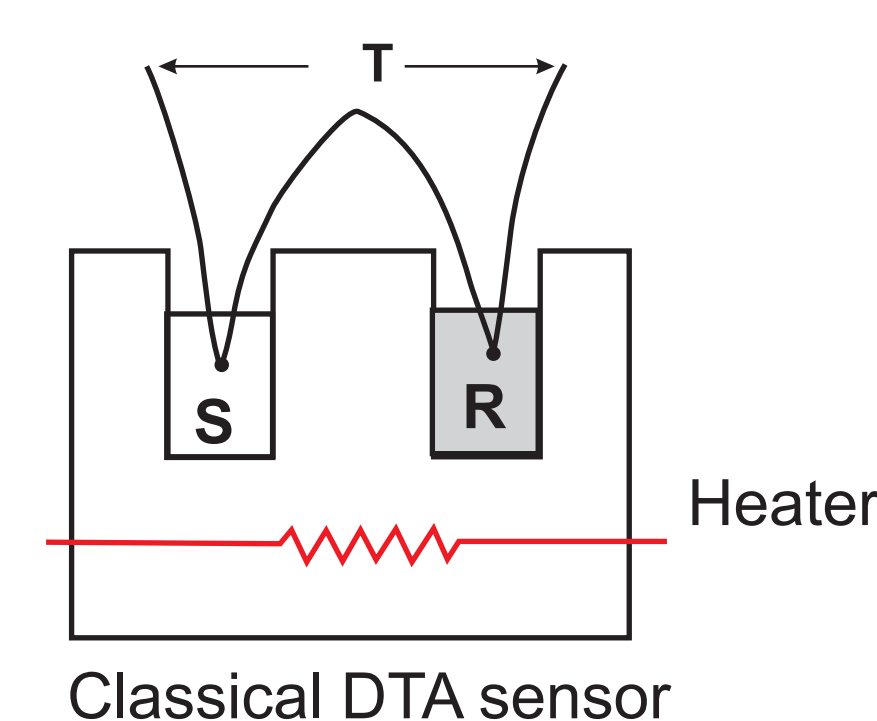
STA 409 STA 449 DSC 404



STA 409 DTA/TG coupled with MS for EGA. Temperature range: RT to 1450 °C. Heating rate up to 30 °C/min.

STA 449 DSC/TG coupled with Bruker FTIR for EGA. Temperature range: RT to 1650 °C. Heating rate: up to 30 °C/min below 1400 °C, up to 20 °C/min above 1400 °C, Cp - measurement range: RT to 1400 °C. Cp accuracy ~5%. Enthalpy accuracy $\pm 3\%$.

DSC 404 Temperature range: -110 to 300 °C or RT to 1500 °C. Heating rate: up to 30 °C/min below 1400 °C.



Research Examples

Thermochemistry of iron oxides

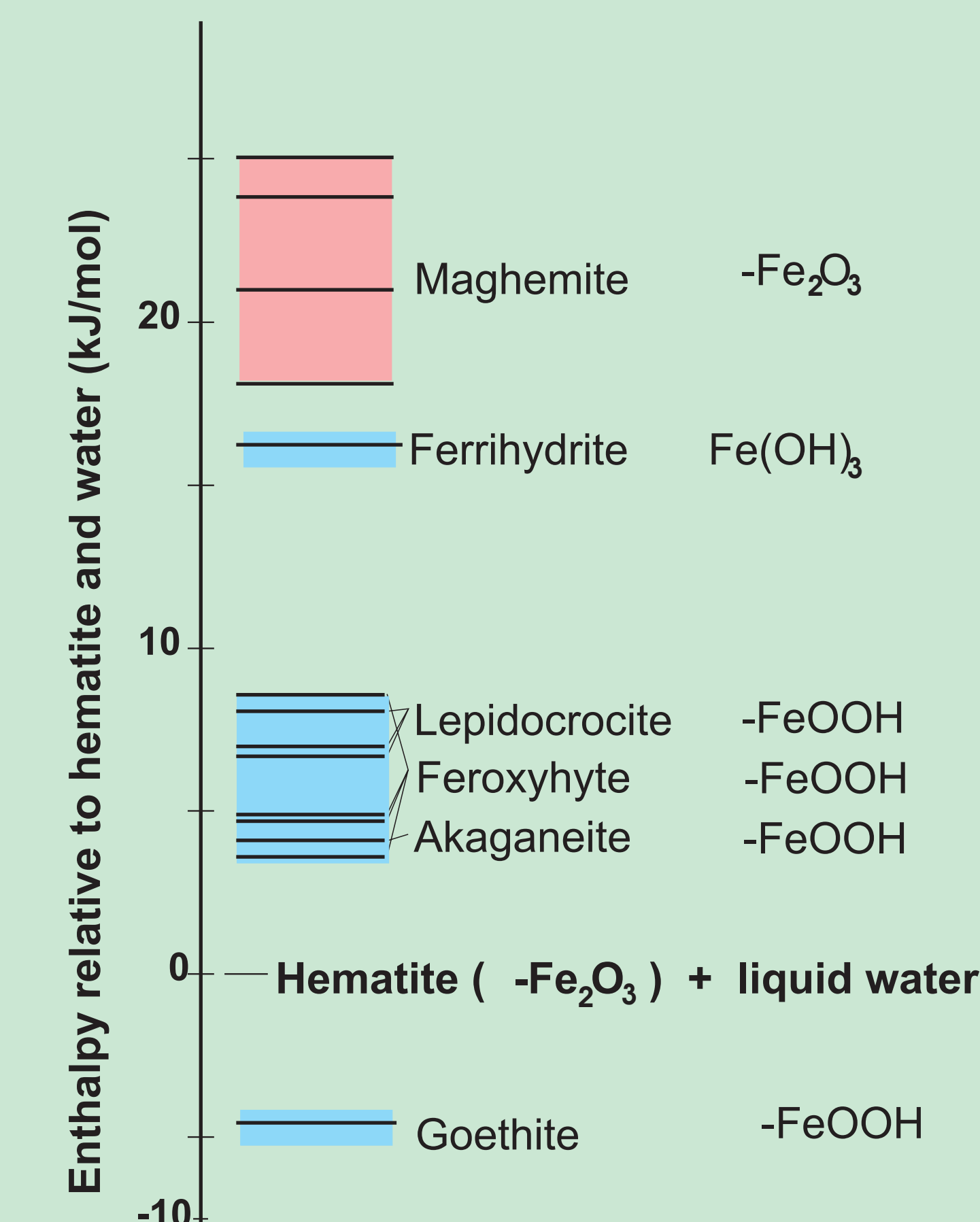
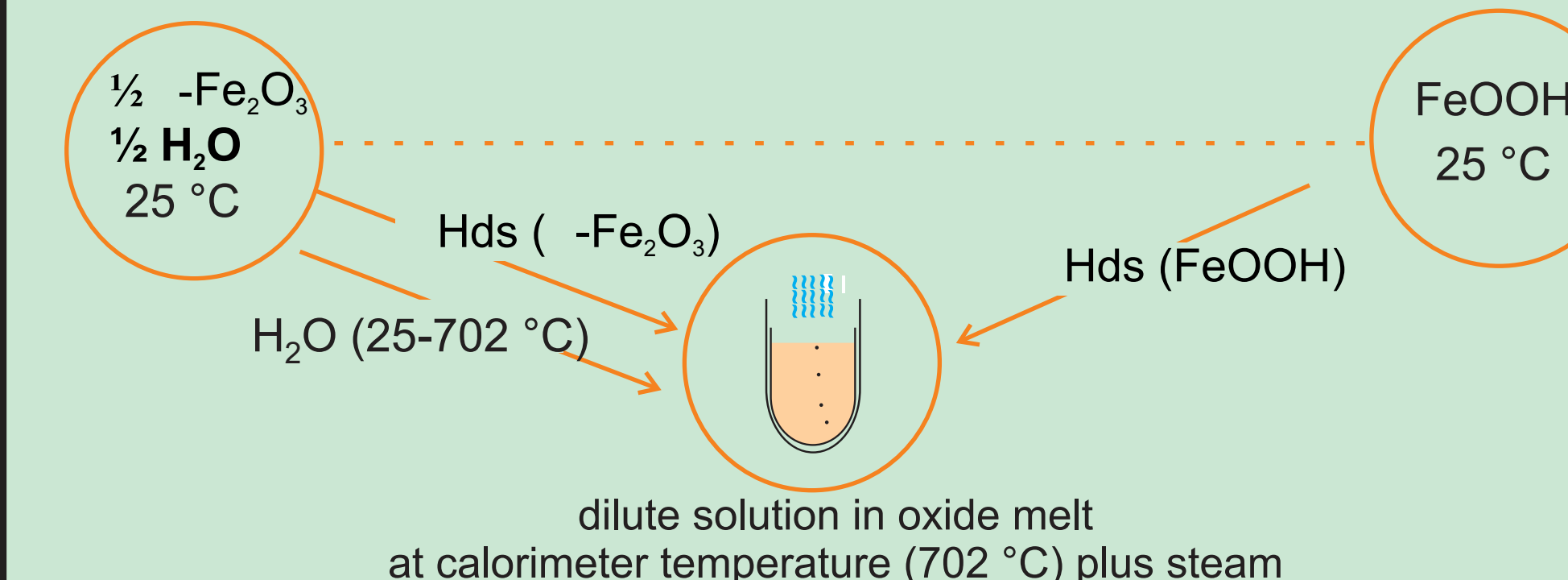
(based on J. Majzlan Ph.D. thesis, 2002)

Thermochemistry of iron oxides and hydroxides is of interest due to their wide use in industry (e.g., use of maghemite as magnetic storage medium in computer hard drives) and widespread occurrence in nature. Samples were synthesized in the Thermochemistry Facility using low-temperature and hydrothermal routes. Structural parameters, composition, and water content were determined using electron microprobe, ICP, thermal analysis, and Rietveld refinement. Drop solution enthalpies were measured by high-temperature oxide melt solution calorimetry using sodium molybdate and lead borate solvents, and the formation enthalpies were calculated using a thermochemical cycle similar to the one shown below.

Example of thermochemical cycle for calculation of enthalpy changes for FeOOH polymorphs relative to Fe_2O_3 and water.

(1) $\text{FeOOH}(\text{cr}, 25^\circ\text{C}) = (\text{solution} + \text{steam}, 702^\circ\text{C})$ $H_{ds}(\text{FeOOH})$
(2) $-\text{Fe}_2\text{O}_3(\text{hematite}, 25^\circ\text{C}) = (\text{solution}, 702^\circ\text{C})$ $H_s(-\text{Fe}_2\text{O}_3)$
(3) $\text{H}_2\text{O}(\text{liquid}, 25^\circ\text{C}) = \text{H}_2\text{O}(\text{steam}, 702^\circ\text{C})$ (from literature)

(4) $\frac{1}{2} -\text{Fe}_2\text{O}_3(\text{hematite}, 25^\circ\text{C}) + \frac{1}{2} \text{H}_2\text{O}(\text{liquid}, 25^\circ\text{C}) = \text{FeOOH}(\text{cr}, 25^\circ\text{C})$
 $H(4) = \frac{1}{2} H(2) + \frac{1}{2} H(3) - H(1)$



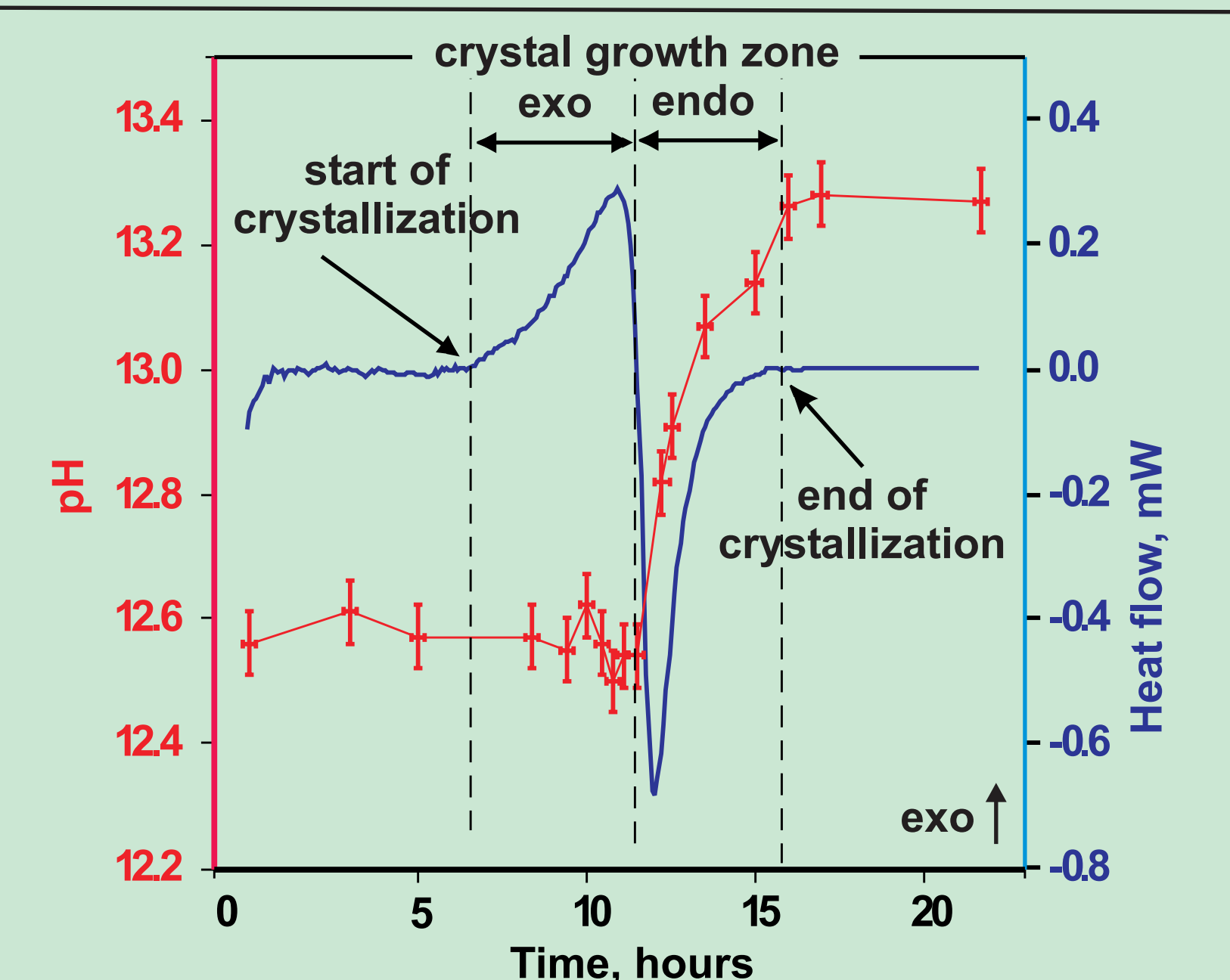
Enthalpy difference of the studied samples w.r.t hematite and liquid water. The refined formation enthalpies fill the gaps in thermochemical data for the system $\text{H}_2\text{O} - \text{Fe}_2\text{O}_3$. Small enthalpy differences among the different FeOOH polymorphs point at the importance of kinetic factors in the formation of these phases.

J. Majzlan, K.-D. Grevel, A. Navrotsky, *Thermodynamics of iron oxides. II. Enthalpies of formation and relative stability of goethite (alpha-FeOOH), lepidocrocite (gamma-FeOOH), and maghemite (gamma-Fe₂O₃).* *American Mineralogist* (submitted 2003).

Thermochemical insight into zeolite crystal growth

Formation of TPA-MFI crystals at 95 °C by orderly aggregation of the pre-assembled 3 nm primary particles (PPs) present in the initial clear solution (9TPAOH - 25SiO₂ - 480H₂O - 100C₂H₅OH, TPA = tetrapropylammonium) is studied by in situ calorimetry using a Setaram C80 calorimeter. In the exothermic crystal growth stage, crystal growth and elimination of surface area apparently cause little change in solution pH, implying an increase of surface charge density. When this increase can no longer be tolerated energetically, hydroxyl is removed from the surface into solution, leading to the switch to endothermic crystal growth and rise in solution pH. The driving force during the late stages of reaction is the entropy of releasing OH⁻ into solution. Thus calorimetry gives direct insight into zeolite crystal self-assembly.

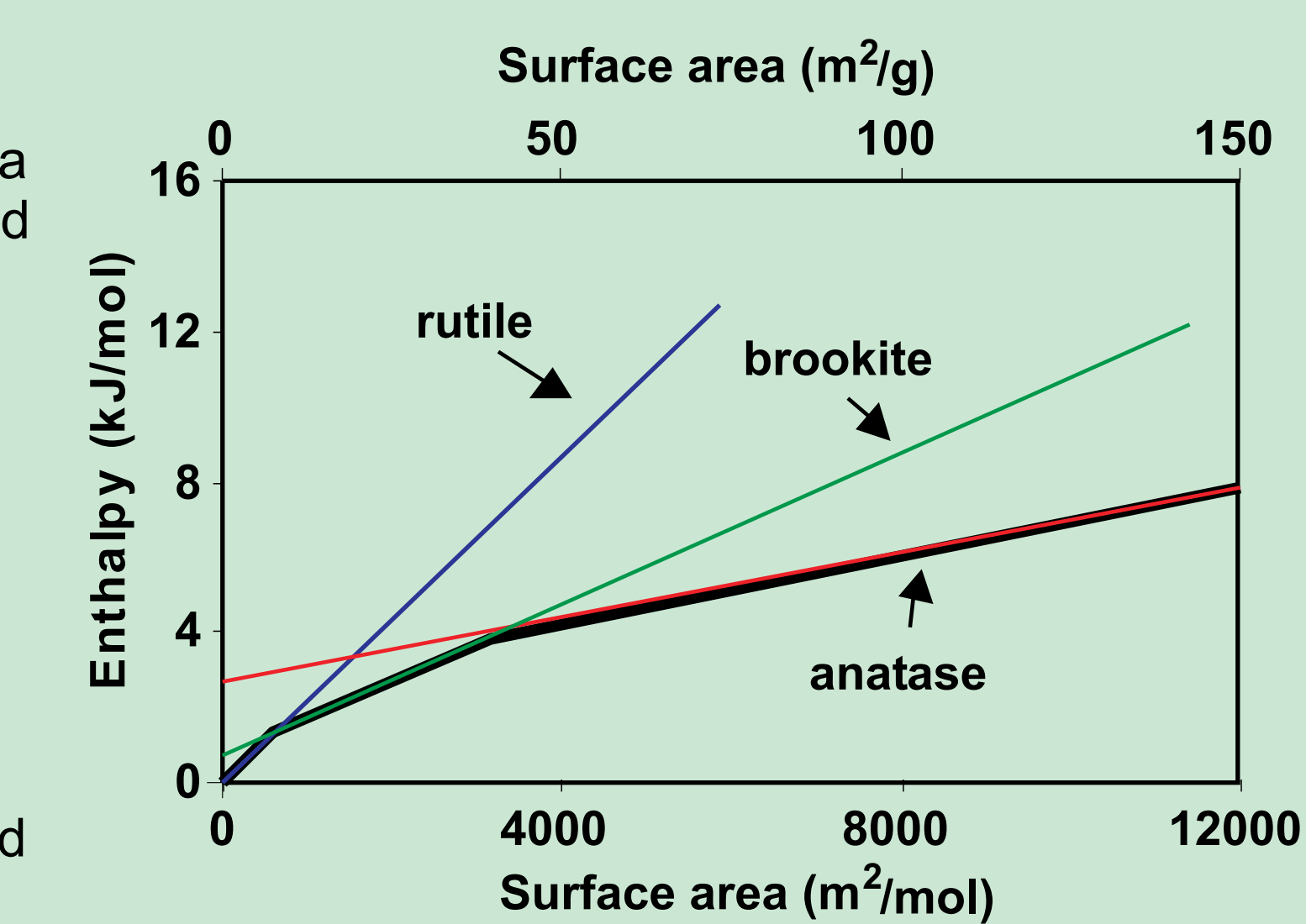
S. Yang, A. Navrotsky, *Chem Mater* 14 (2002) 2803



Particle size effects on energetics of TiO₂ polymorphs

(based on M. Ranade Ph.D. thesis, 2002)

It has long been observed that fine grained oxides precipitated from aqueous solution often crystallize in structures different from that of coarsely crystalline materials: gamma alumina instead of corundum, anatase and brookite instead of rutile, maghemite instead of hematite, and a host of complex hydrous iron oxyhydroxides. It has also been suspected that differences in surface energy may stabilize, as nanoparticles, polymorphs that are metastable in the bulk. High temperature oxide melt solution calorimetry has directly confirmed this crossover in energetics for - versus -alumina (McHale et al. 1997). Nanocrystalline anatase, brookite, rutile, and mixtures of anatase and rutile have been studied using high temperature molten oxide drop solution calorimetry at 975 K with $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ solvent using a Calvet type twin microcalorimeter (Ranade et al. 2002). The transformation enthalpies for bulk (coarse) materials (anatase-rutile and brookite-rutile) and the surface enthalpies were derived from the calorimetric data. Relative to bulk rutile, bulk brookite is 0.71 ± 0.38 kJ/mol and bulk anatase is 2.61 ± 0.41 kJ/mol higher in enthalpy. The surface enthalpies of rutile, brookite, and anatase are 2.2 ± 0.2 J/m², 1.0 ± 0.2 J/m², and 0.4 ± 0.1 J/m² respectively. The closely balanced energetics directly confirm the crossover in stability of nanophase polymorphs inferred by Zhang and Banfield (1998).



J. M. McHale, A. Auroux, A. J. Perrotta, and A. Navrotsky (1997) *Surface energies and thermodynamic phase stability in nanocrystalline aluminas.* *Science* 277, 788-791; M.R. Ranade, A. Navrotsky, H.Z. Zhang, J.F. Banfield, S.H. Elder, A. Zaban, P.H. Borse, S.K. Kulkarni, G.S. Doran, and H.J. Whitfield (2002) *Energetics of nanocrystalline TiO₂.* *Proc. Nat. Acad. Sci.* 99, suppl 2, 6476-6481; H. Zhang and J.F. Banfield (1998) *Thermodynamic analysis of phase stability of nanocrystalline titania.* *J. Mater. Chem.* 8, 2073-2076