



# PHASE TRANSFORMATIONS AS IMPORTANT MARKERS FOR HEAT TREATMENT DETECTION OF CORUNDUM AND OTHER GEMSTONES

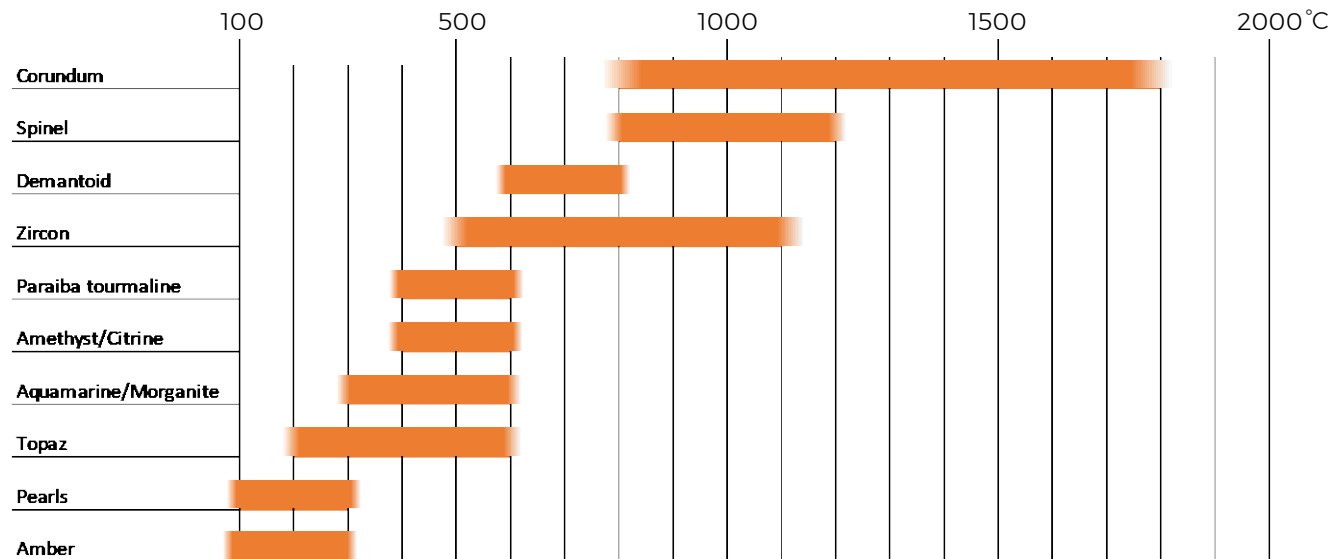
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# HEAT TREATMENT OF GEMSTONES

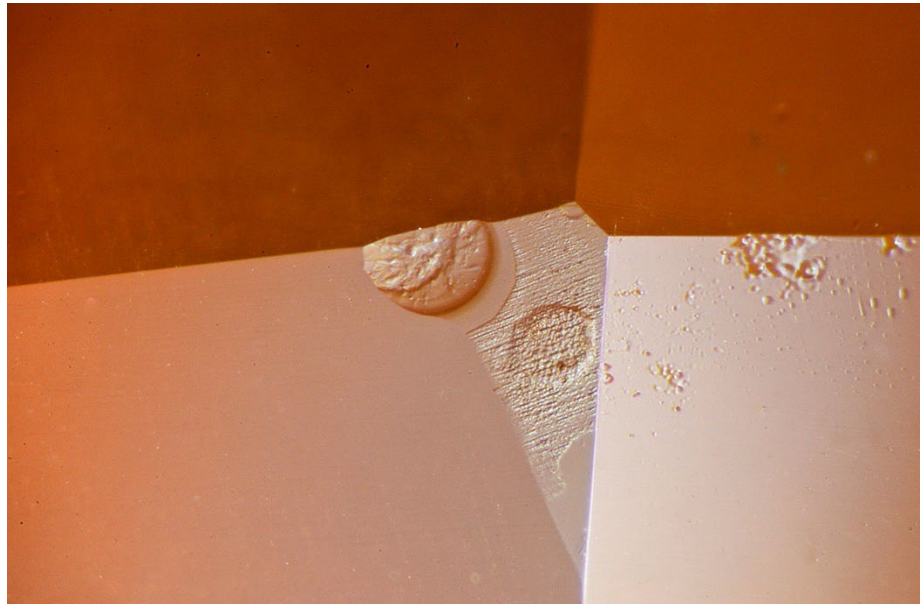


*approx. temperature ranges as by gemmological literature*

- Depending on the gemstone, different heating temperatures are required to result in an enhancement.
- In most cases, heat treatment results in a change/shift of colour.
- In certain cases may also reduce turbidity or create other desired (optical) effects.

# | DETECTION OF HEATING:

## Microscopy

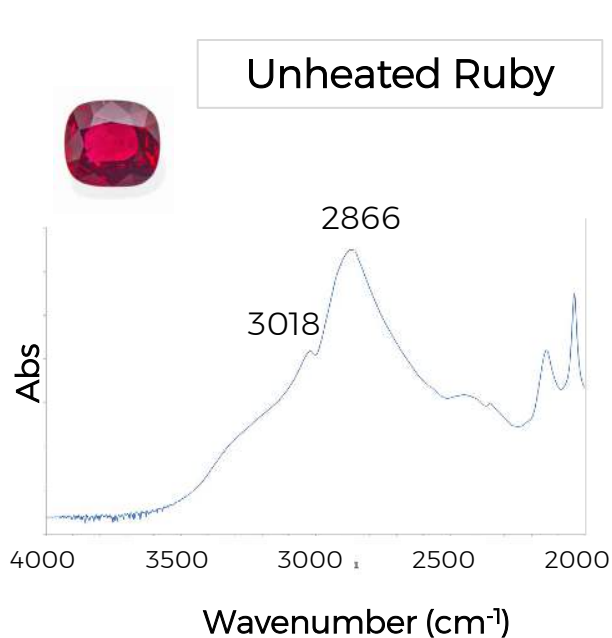


Atoll-structures (discoid extension features) and “burn marks” at the surface are proof of a heat treatment in this orange sapphire.

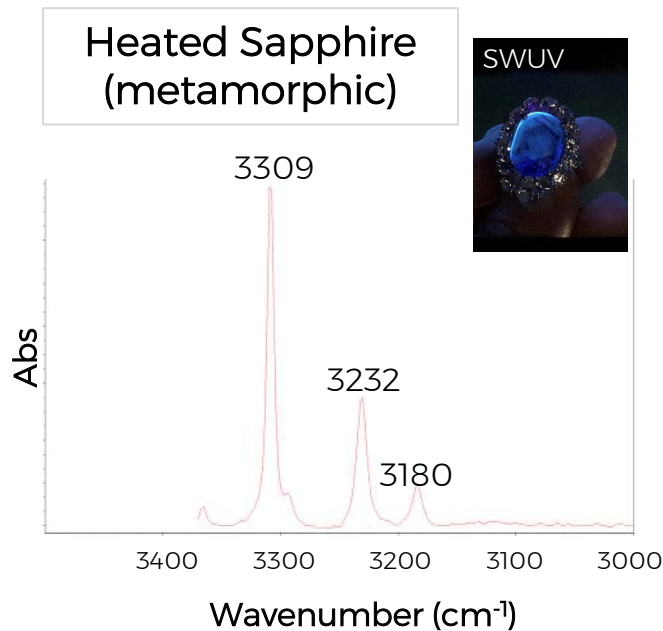
However, such features indicating heating are often absent, specifically in stones heated at lower temperatures (< 1000 °C)

# DETECTION OF HEATING

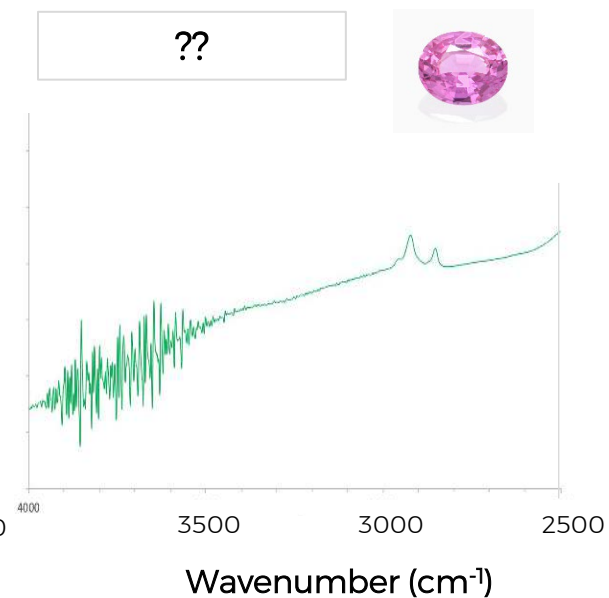
## FTIR Spectroscopy of Corundum



Diaspore related bands



Ti<sup>4+</sup>- OH<sup>-</sup> related peaks

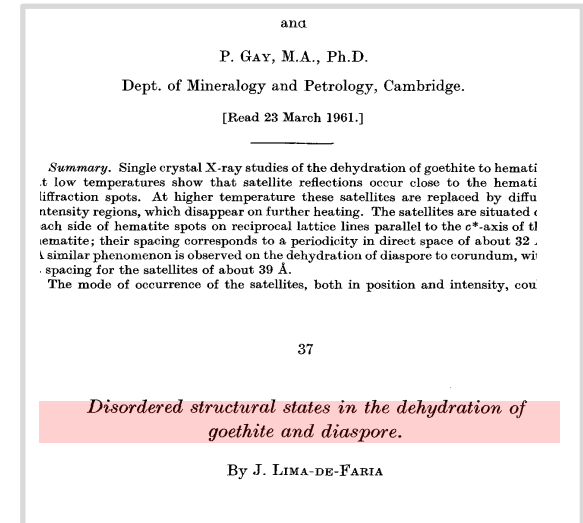


No signal indicating heat or no heat

# PHASE TRANSFORMATIONS

Classic examples:

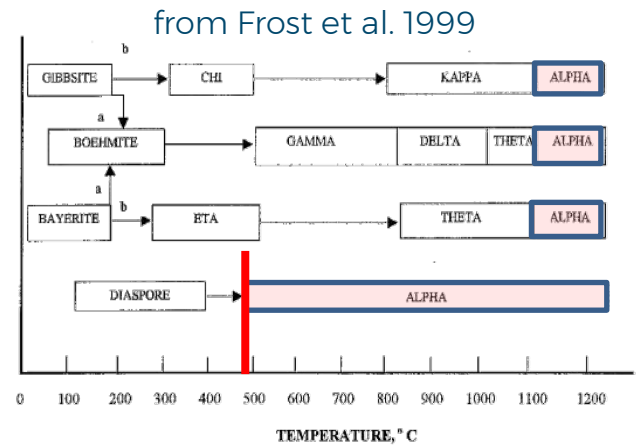
Diaspore ( $\alpha$ -AlOOH) and Goethite ( $\alpha$ -FeOOH)



Dehydration of diasporite and goethite is known and has been studied for many decades (Deflandre, 1932; Goldsztaub, 1935; Rooksby, 1951; Ervin, 1952; Francombe and Rooksby, 1959, etc).



# PHASE TRANSFORMATIONS



## Dehydration of diaspore to corundum:

De Faria & Gay P. 1963:

400 °C (heated 20 days); 550 °C (heated ~20 minutes)

Iwai et al. 1973:

550 °C (heated 1 hour)

Carim et al. 1997:

above 400 °C (138 h)

Annealing in air: direct and more rapid than in vacuum!

Frost et al. 1999:

500 to 530 °C over small temperature range!

## Dehydration of goethite to hematite:

De Faria & Gay P. 1963:

300 °C (heated 19 h); 351 °C (heated ~20 minutes)

Pomiès et al. 1998:

250 to 270 °C

Ruan et al. 2002:

250 to 300 °C

de Faria & Lopes 2007:

300 °C (regardless if 1 or 40 hours)

however rather large bandwidths (lower crystallinity)

Wells et al. 2006:

250 to 300 °C

Al-substituted goethite at slightly higher temperatures

# PHASE TRANSFORMATIONS



from Koivula 2013

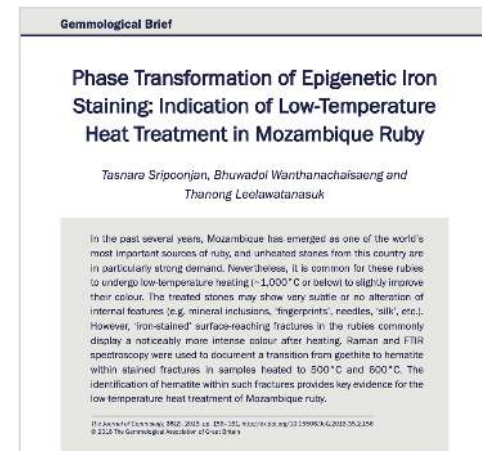
## Gemmological literature:

Koivula J.I. 1987: Goethite inclusion alteration during the heat conversion of amethyst to citrine. *The Australian Gemmologist*, Vol. 16, No. 7, pp. 271-272.

Kammerling R.C. & Koivula J.I., 1989. Thermal alteration of Inclusions in “rutilated” topaz. *Gems & Gemology*, 25, 3, 165-167. <http://dx.doi.org/10.5741/GEMS.25.3.165>

Koivula J.I., 2013. Useful visual clue indicating corundum heat treatment. *Gems & Gemology*, 49, 3, 160-161. <http://dx.doi.org/10.5741/GEMS.49.3.160>

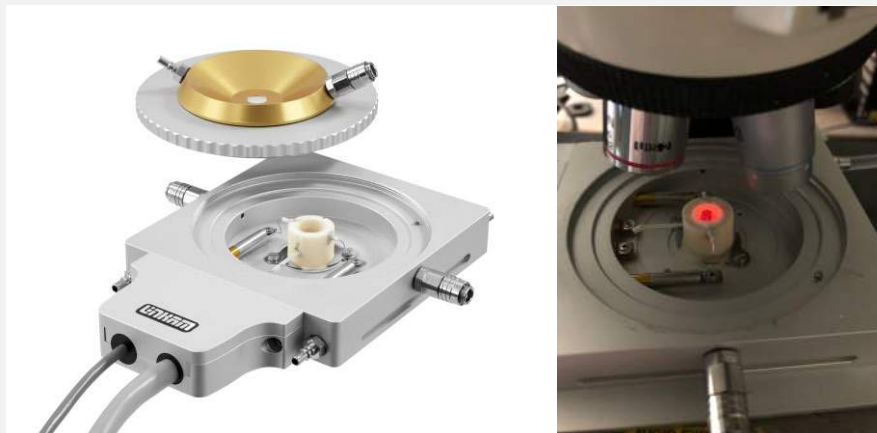
Sripoonjan et al. 2016: Phase transformation of epigenetic iron staining: In dication of low-Temperature heat treatment in Mozambique ruby. *JoG*, 35 (2), 156-161.



Sripoonjan et al. 2016

# HEATING EXPERIMENT

Heating stage Linkam TS 1200  
- Coupled with Raman system  
for in-situ measurements



Step-wise heating,  
 $T_{\max}$  per step kept for 4 minutes only

Electric muffle furnace  
Nabotherm LHT 18  
- Heating similar to gem trade








Step-wise heating,  
 $T_{\max}$  per step kept for 1 hour

Heating in air, step-by-step heating, Raman spectra only after cooling down

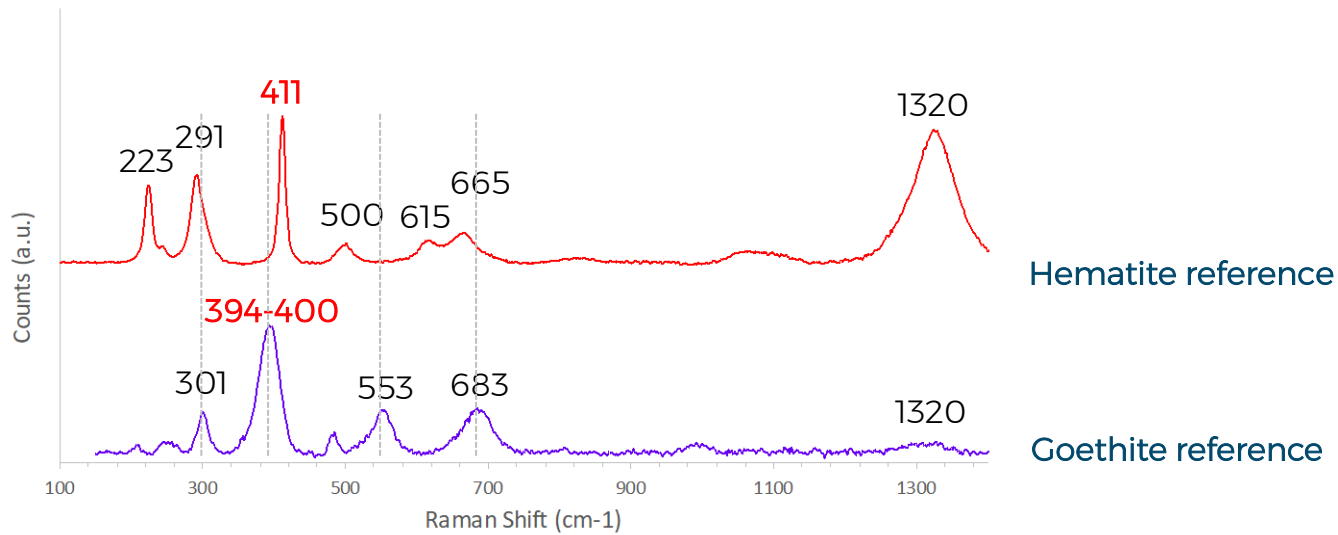
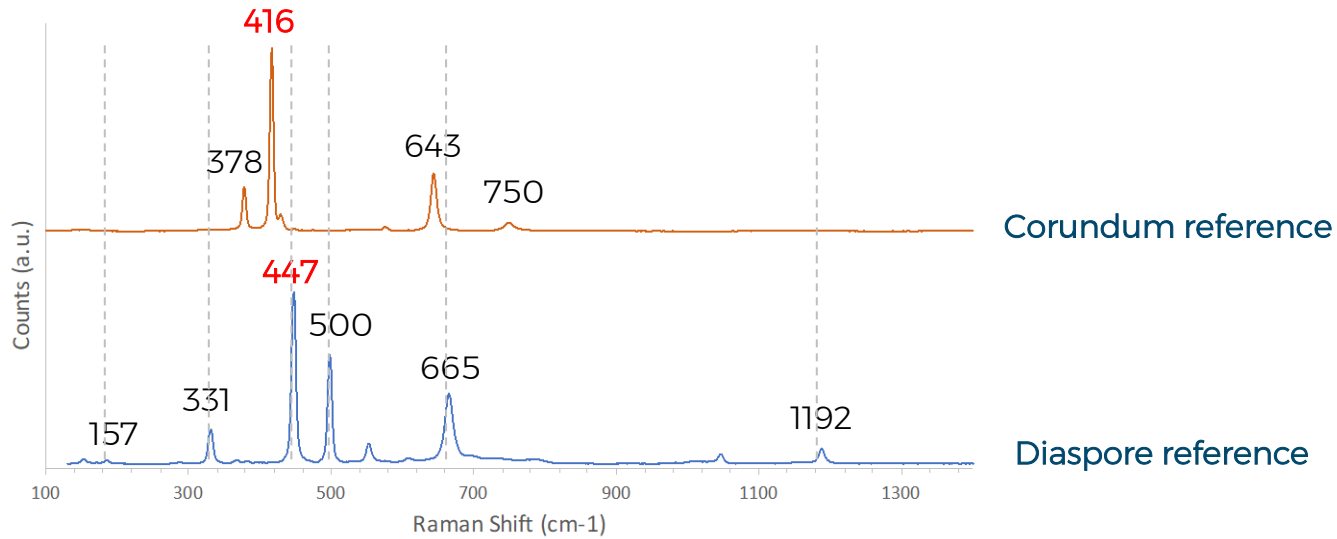


# HEATING EXPERIMENT

Sample		ID	Weight (ct)	Shape	Colour	Origin	Heating	max T °C	Colour after Heating
97003		Diaspore	0.40	flat fragment	colourless	Muğla Prov., Turkey	Electric furnace	800	whitish
126993_6		Ruby with diaspore	0.19	polished slab	red	Mogok, Myanmar	Heating stage	700	no change
106424_21		Sapphire with diaspore	1.03	faceted	blue	Mogok, Myanmar	Heating stage	700	no change
85933_C3		Ruby with goethite	0.52	polished slab	red	Montepuez, Mozambique	Heating stage	400	no change
120553_B		Ruby with goethite	1.31	polished slab	red	Montepuez, Mozambique	Electric furnace	1000	no change

Important: none of the corundum samples showed any change of colour after our heating experiments reaching a maximum of 1000 °C.

# RAMAN SPECTRA OF PHASES

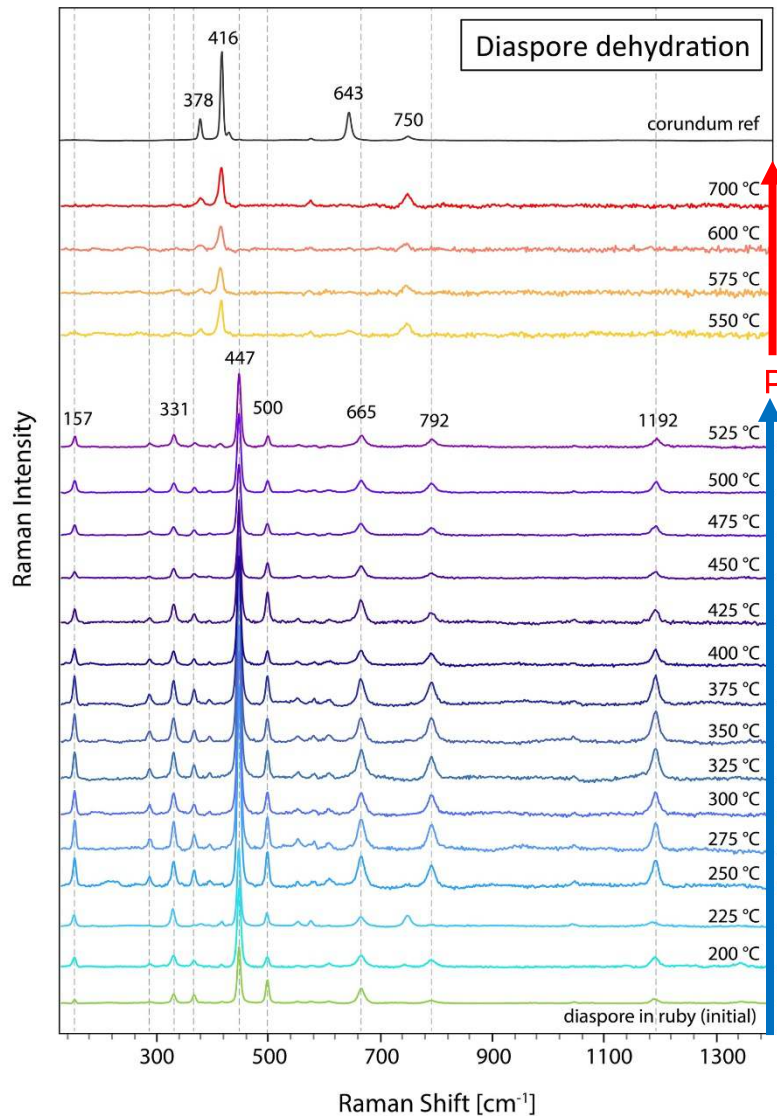


# DIASPORE TO CORUNDUM



Sample 120993\_6  
Diaspore in Burmese ruby (Mogok)

Experiment setup:  
Linkam heating stage



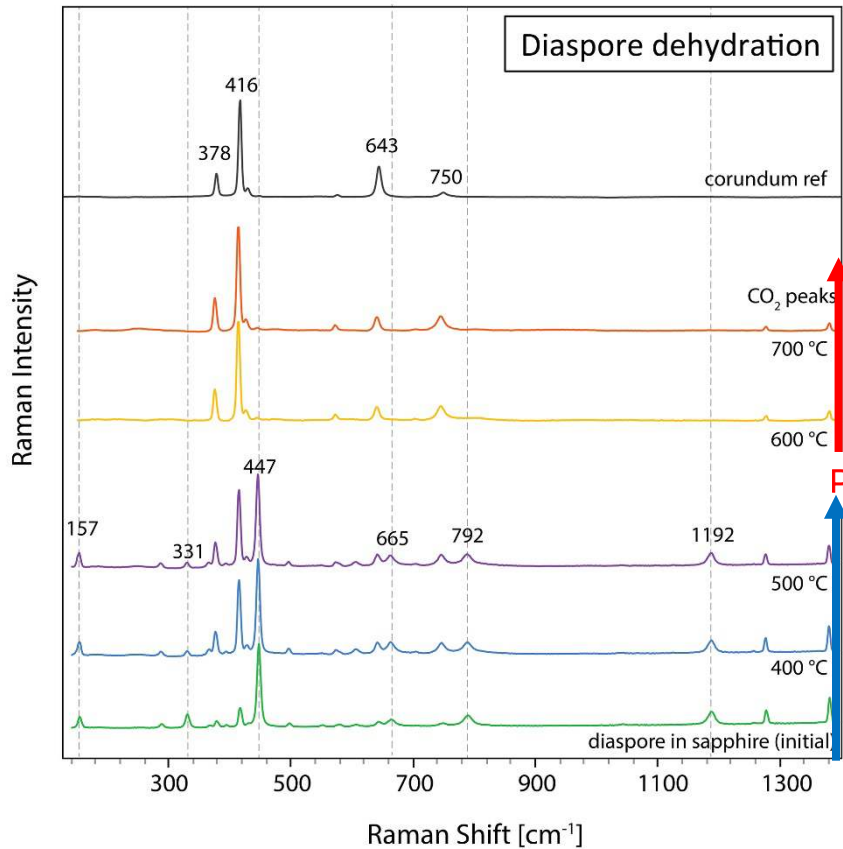
Phase transformation



Diaspore in ruby (image width 2mm).

dotted vertical lines: main diaspore peaks

# DIASPORE TO CORUNDUM

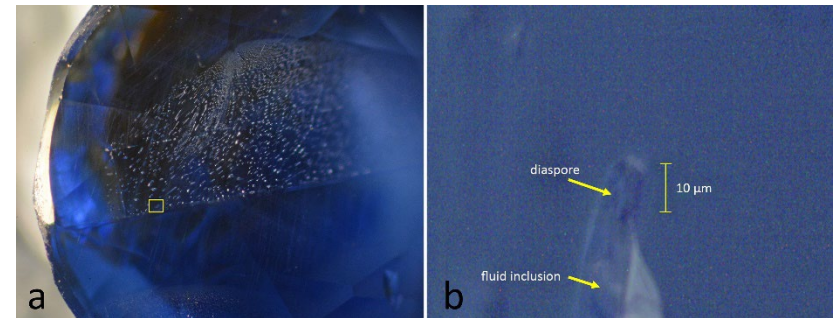


dotted vertical lines: main diaspore peaks

Sample 106424\_21  
Diaspore in Burmese sapphire (Mogok)

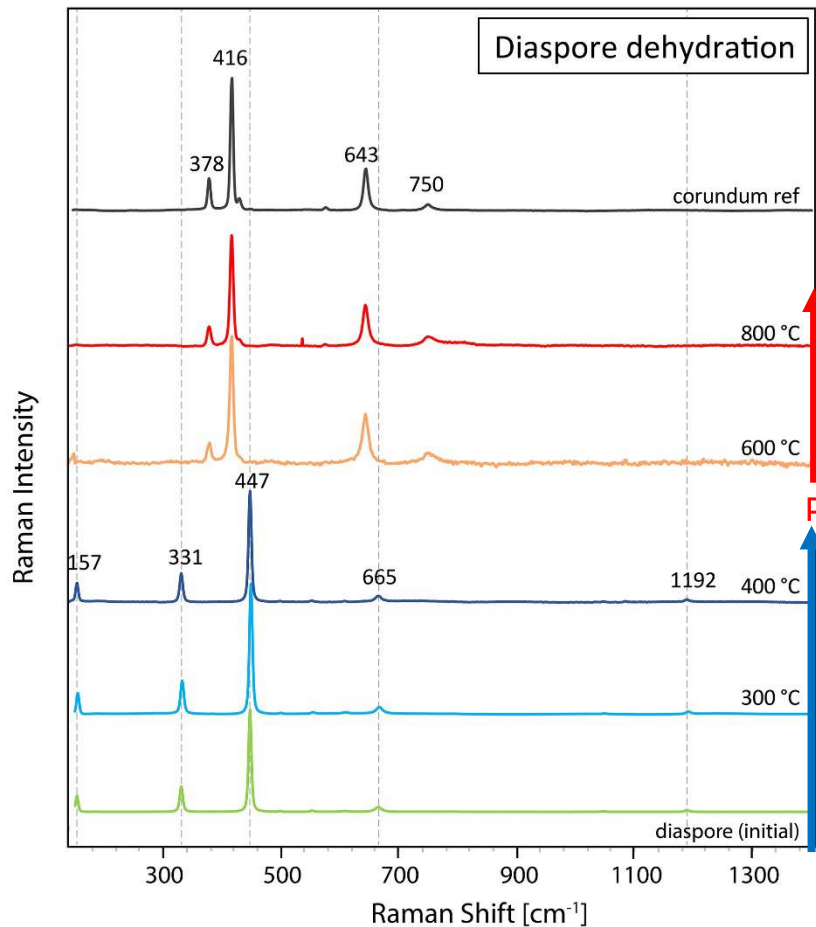
Experiment setup:  
Linkam heating stage

Phase transformation



Diaspore in fluid inclusion in sapphire  
(approx. 10  $\mu\text{m}$ ).

# DIASPORE TO CORUNDUM



Sample 97003  
Diaspore from Muğla Province, Turkey

Experiment setup:  
Electric muffle furnace (Nabotherm)

Phase transformation



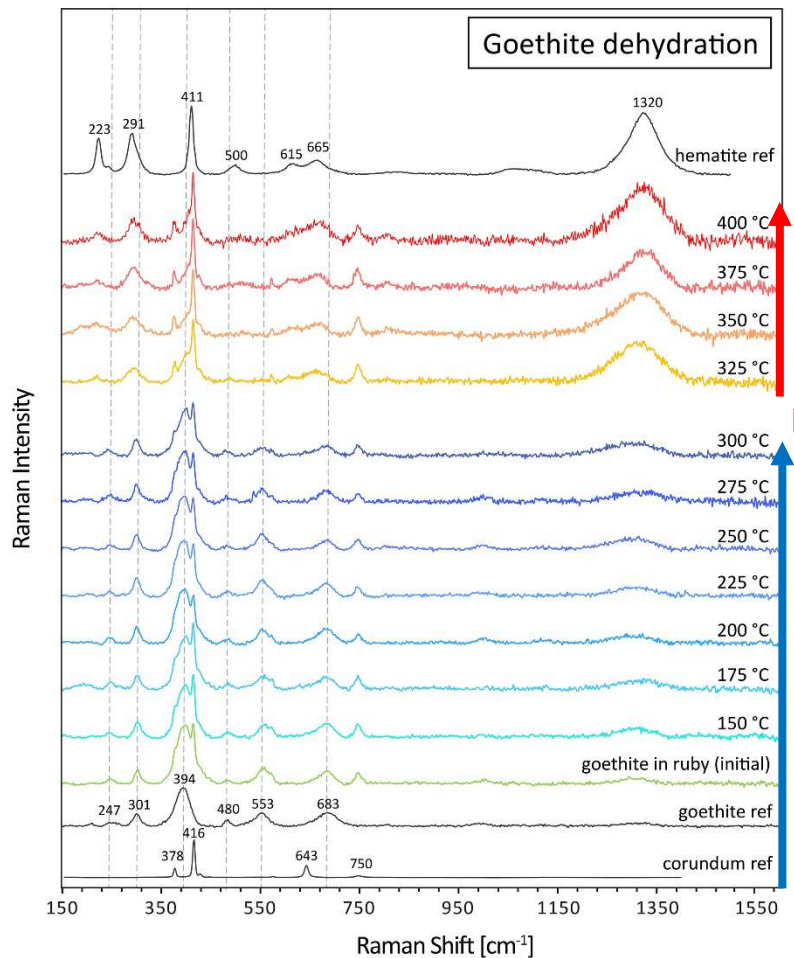
dotted vertical lines: main diaspore peaks

# GOETHITE TO HEMATITE

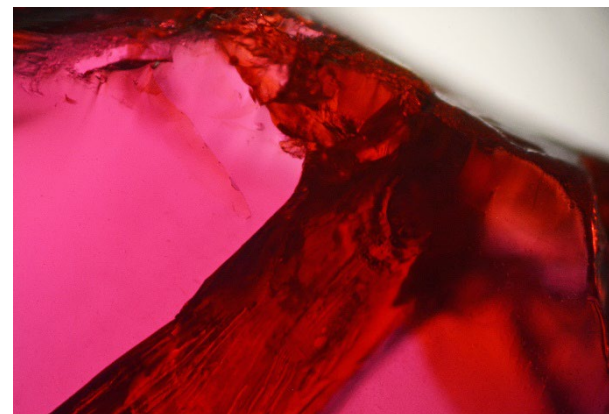


Sample 85933\_C3  
Goethite in Mozambique ruby

Experiment setup:  
Linkam heating stage



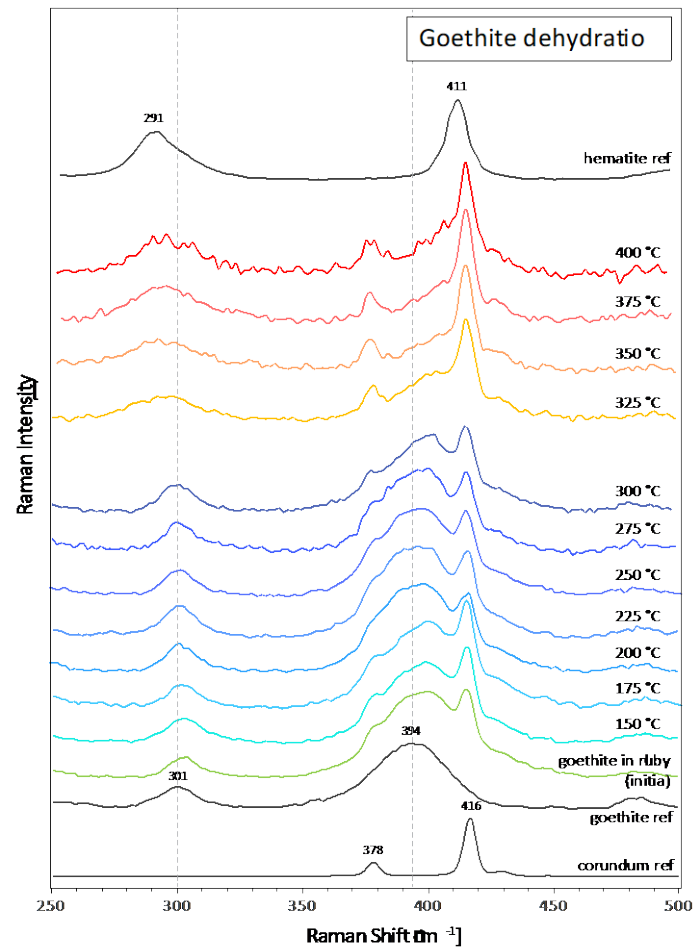
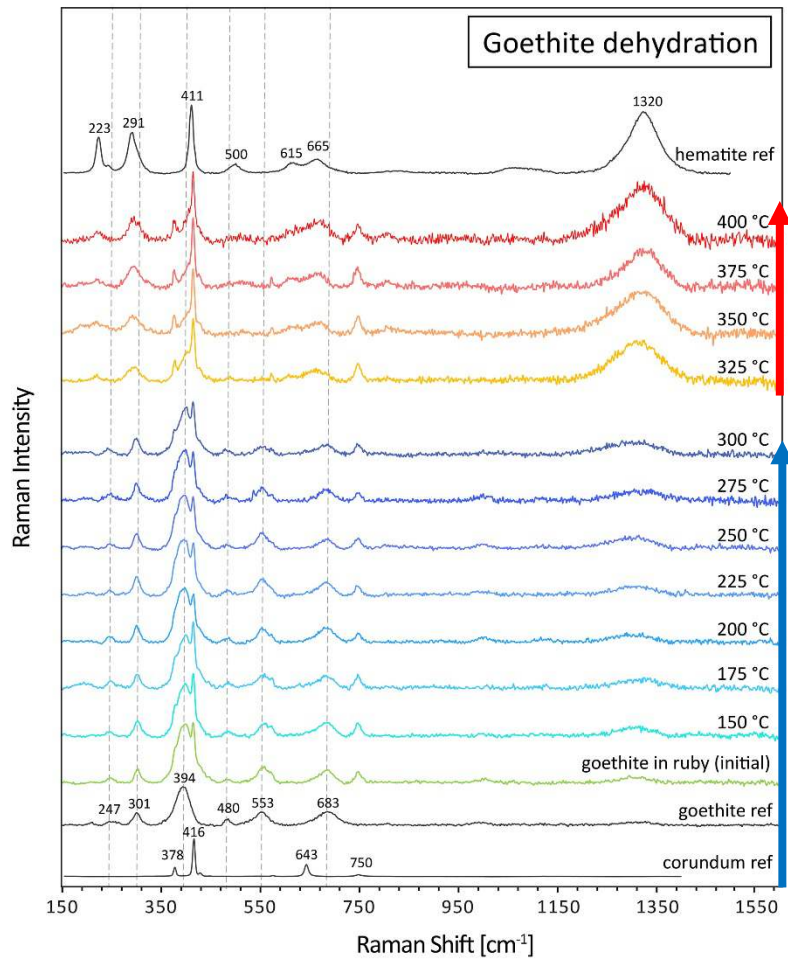
Phase transformation



Goethite in fissure in ruby

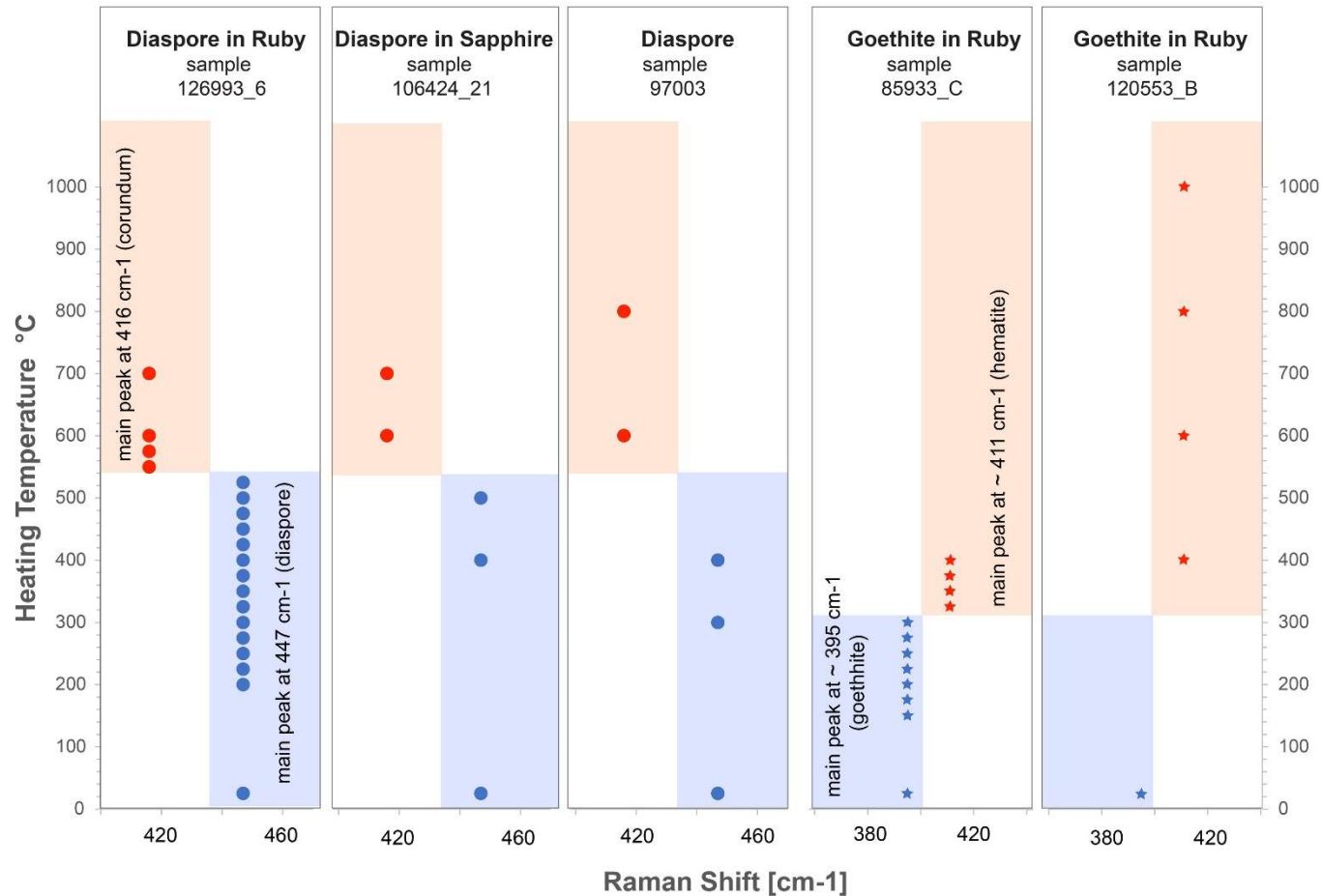
dotted vertical lines: main goethite peaks

# GOETHITE TO HEMATITE



dotted vertical lines: main goethite peaks

# RESULTS OF HEATING EXPERIMENTS

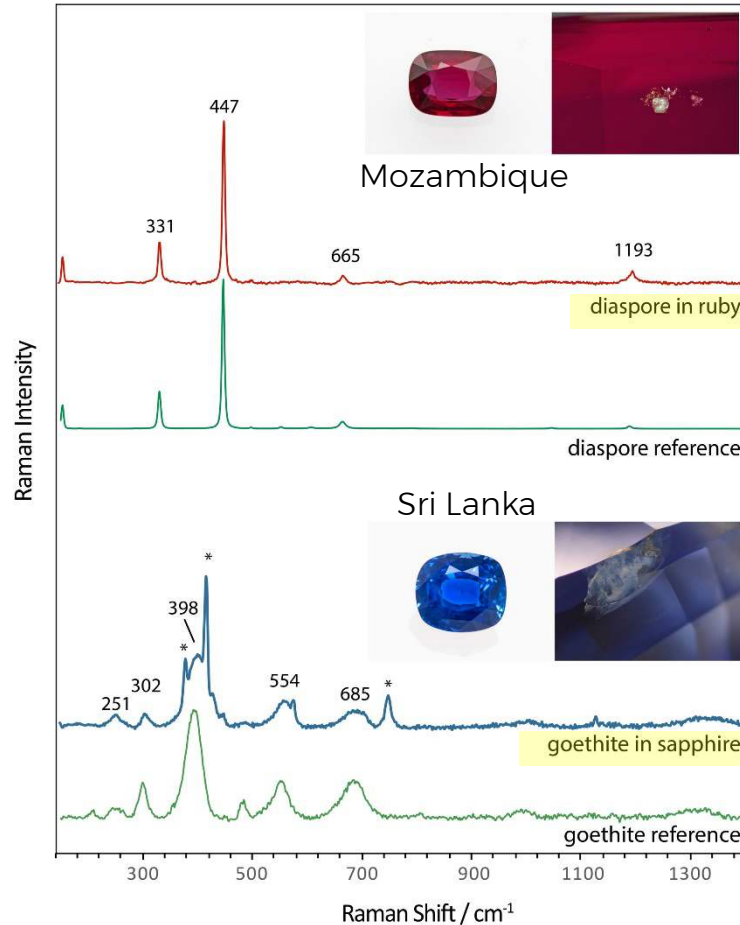


Regardless of size and position of the inclusion, the phase transitions (dehydration) of the diaspore and goethite can be observed in in all samples in their specific temperature range (diaspore about 525 °C; goethite about 325 °C)

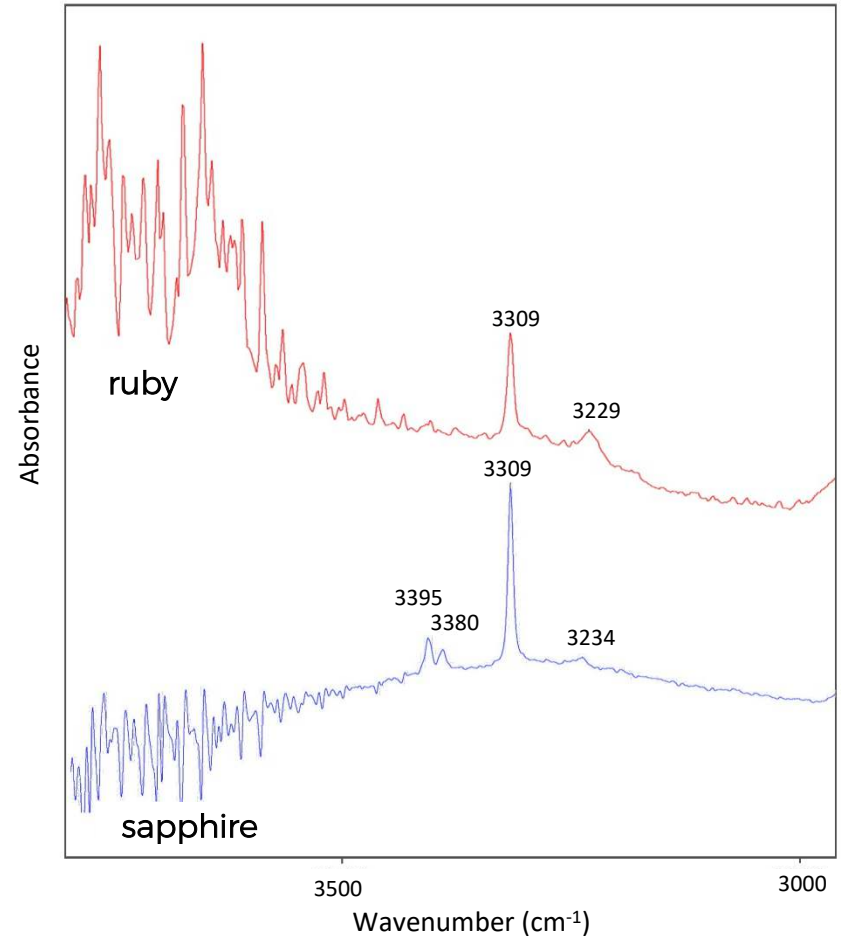


# REAL CASES

## Raman



## FTIR



FTIR can be tricky, the peaks at 3229 and 3234 are not identical with the peak at 3232  $\text{cm}^{-1}$  commonly related to heating !

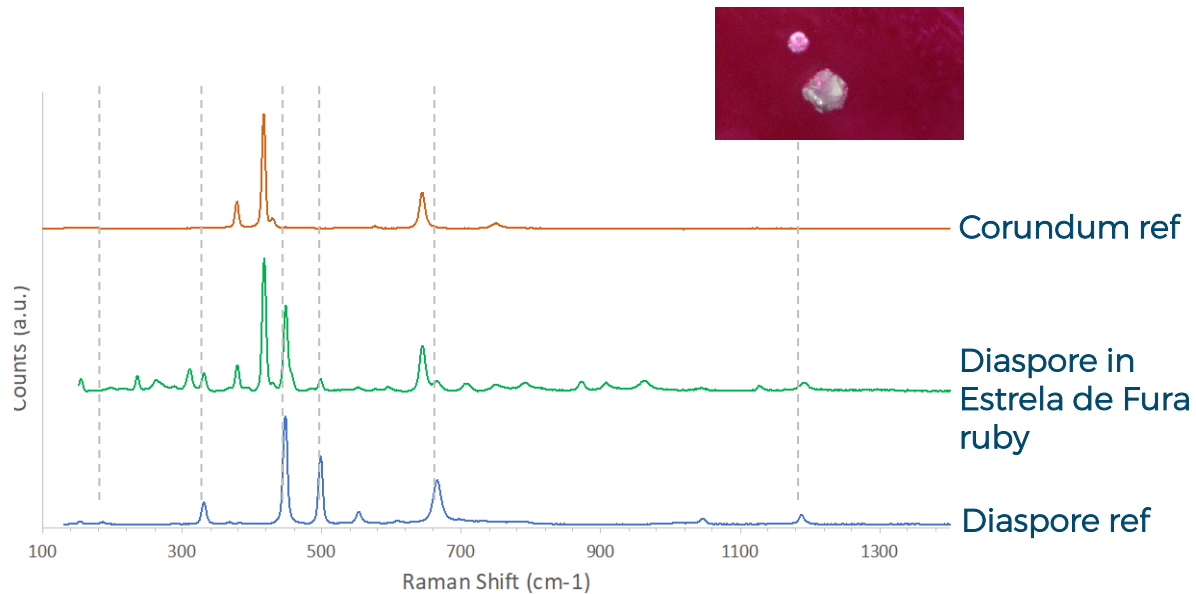
Corundum with similar FTIR spectra have already been identified as heated!

# REAL CASES



Estrela de Fura 55.22 ct

Sells at auction Sotheby's auction June 2023 for record \$34.8 million.



Diaspore detected in fluid inclusion !

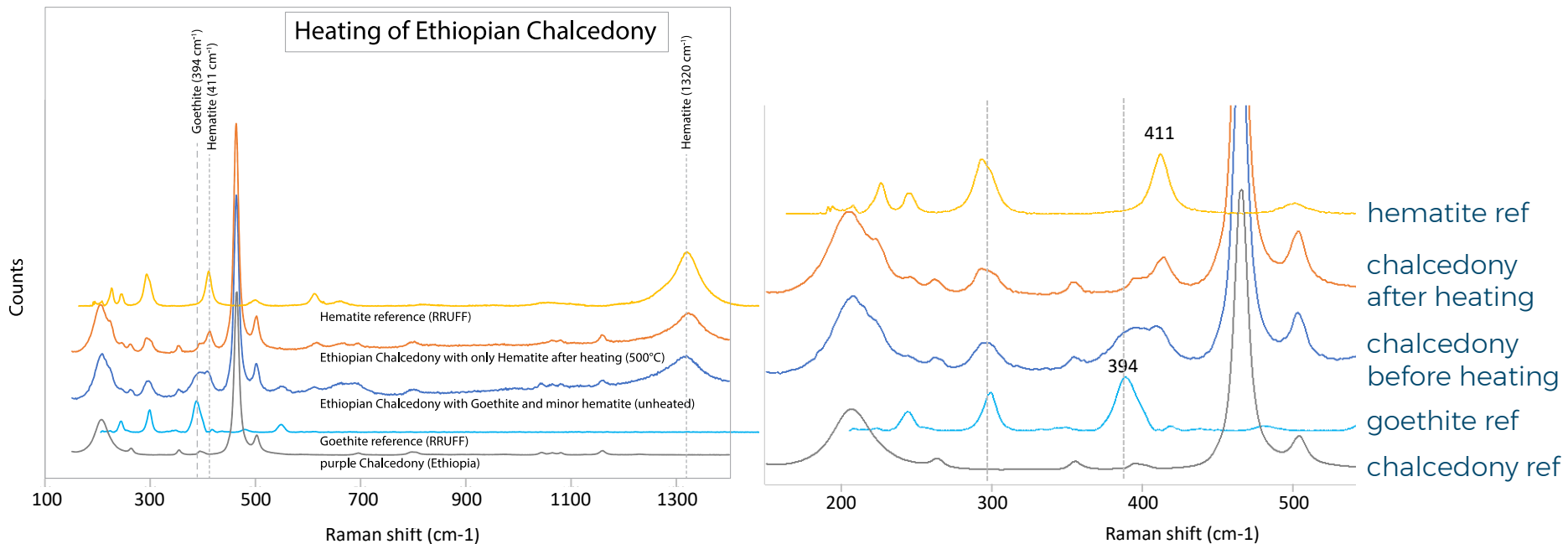


from Sotheby's International

# REAL CASES

## Purple Chalcedony from Ethiopia: Heating Experiment

- 30 minutes for ramping up
- 120 minutes at **500 °C**
- 60 minutes cooling down
- Heating in air



Goethite present in this chalcedony transforms to hematite as a result of heating. Some hematite already present before heating!

# | CONCLUSIONS

- Diaspore and goethite are oxyhydroxides which dehydrate to anhydrous oxides when heated.
- Our experiments confirm phase transformation temperatures as reported in literature (goethite to hematite at  $\sim 325$  °C; diaspore to corundum at  $\sim 550$  °C).
- Phase transformation occurs in small temperature range, thus resulting in a quasi immediate switch in the Raman spectrum.
- Phase transformation cannot be stopped or shifted to higher temperatures, and affects all diaspore and goethite at the same moment.
- The presence of diaspore and/or goethite is a **clear indication**, that a corundum is **not heated** (either by low-T heating  $> 800$  °C), even in cases when FTIR may reveal peaks which could be (mis)interpreted as related to heating or no information whether a stone is heated or not.
- The absence of diaspore or the presence of hematite is not enough to call a stone heated.
- Applicable on all kind of gemstones, as long as diaspore or goethite are present.

THANK YOU FOR YOUR ATTENTION



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