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Multiple Hydrate Structure Formation in Natural Gas Systems: Experimental Measurements and Modelling

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Introduction

While extensive experimental data & modelling capabilities exist for phase boundaries for complex hydrate systems, phase behaviour in the hydrate region is less well constrained.

In real situations, hydrates may form at high ΔT

- Multiple stable / metastable phases can grow
- Dissociate / reform
- Gas fractionation drives new structures

In related posters, it is described how multiple structure formation is apparently linked to:

- Agglomeration / plugging / transportability tendency
- AA & KHI performance
- Can also be expected in sedimentary hydrate systems, e.g. gas production / CO₂ injection
- Seen in simulated flue gas sequestration tests

Results & Discussion

We present isochoric equilibrium PVT and QCM (quartz crystal microbalance) data which supports:

- Multiple hydrate phases / structures at equilibrium as ΔT / hydrate fraction increases
- Depending on growth PT pathways, persistent structural hysteresis can occur
- QCM studies support structural changes at higher ΔT , including for pure C₁

Complementary in-house thermodynamic modelling:

- CPA EoS for fluid phases
- Van der Waals & Platteeuw solid solution theory for hydrate
- Predictions agree well with experimental data
- Support the sequential growth of multiple hydrates
- C₃/C₄ s-II > C₂ s-II > s-I > C₁ s-I
- At equilibrium, driven by gas fractionation
- Including low P s-II C₁ hydrate

In addition to equilibrium predictions, boundaries for non-equilibrium *incipient* hydrate formation conditions are also predicted

- Delineate PT conditions where different hydrate structures can form, even if not most stable phase
- As seen in experimental studies: Metastable pure component C₁ grows faster than mixed s-I/s-II
- Important for higher ΔT flow assurance applications
- KHI / AAs, particularly shut-in, cool-down & restart
- S-I cause of failure in s-II NGs!

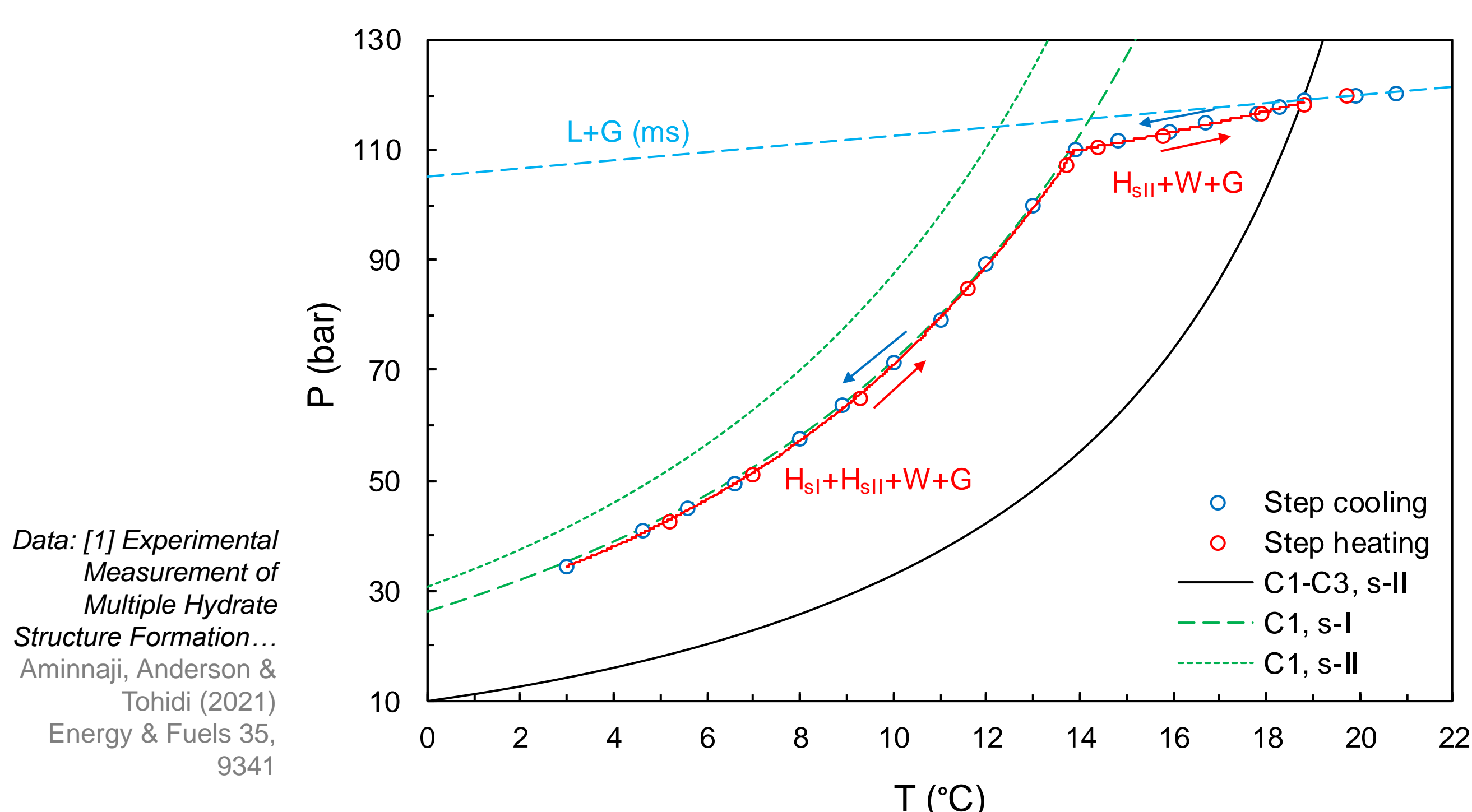


Figure 1 Experimental equilibrium data for 98% C₁ / 2% C₃ vs predicted phase boundaries. While C₁-C₃ s-II is the most stable phase, C₁ s-I hydrate (and even C₁ s-II) is stable at higher ΔT , and comprises the bulk of the hydrate formed at equilibrium once C₃ is completely enclathrated. H = hydrate, W = aqueous, G = gas, ms = metastable.

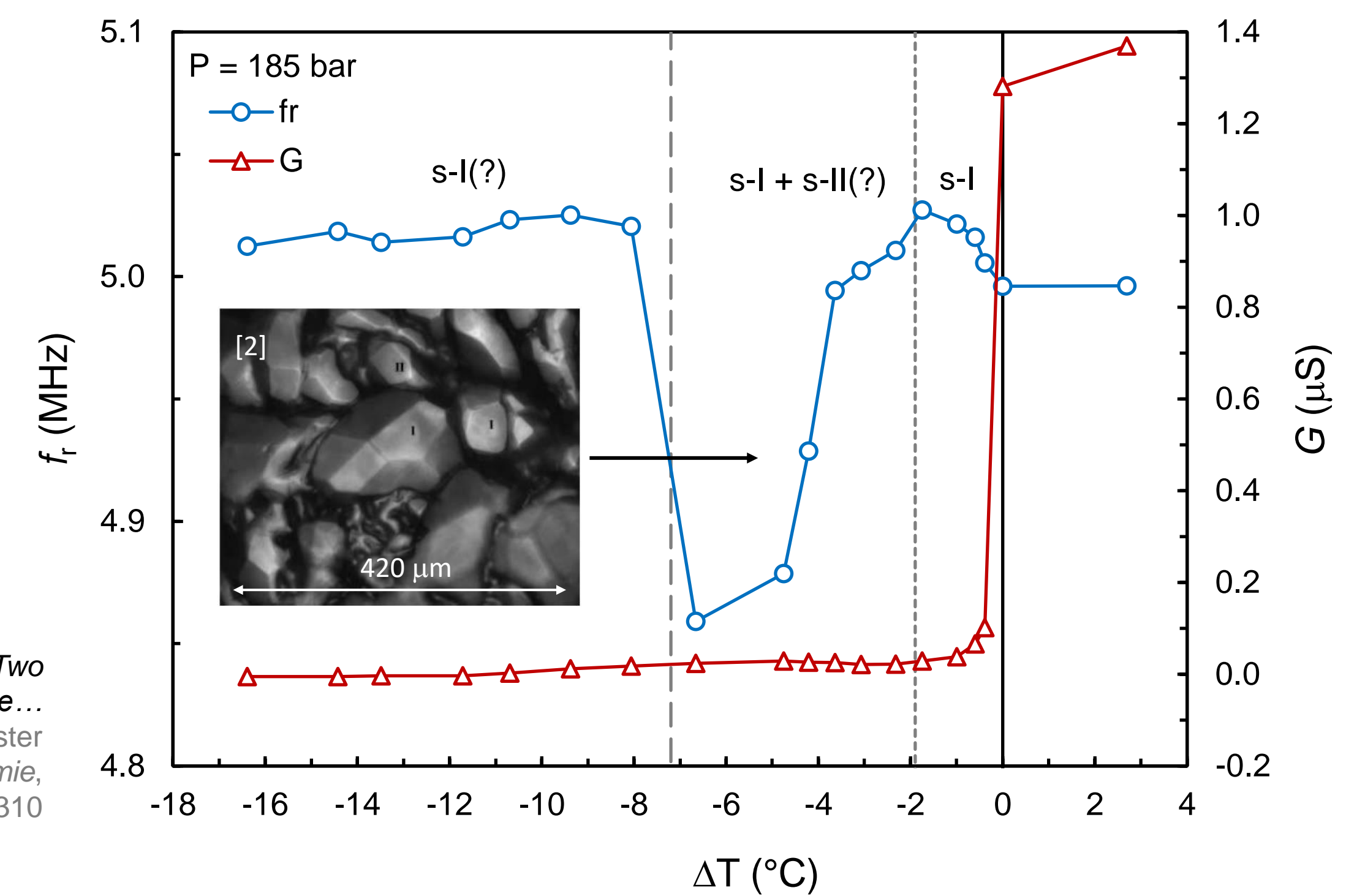


Figure 2. Equilibrium step-heating quartz crystal microbalance (QCM) data for C₁-H₂O. f_r = frequency, G = conductance. In addition to a strong G response during final dissociation, a significant f_r change is observed at modest ΔT where a low-P s-II C₁ hydrate is known [1] and model predicted to form. Given the QCM response is an equilibrium one, data suggest s-II is very stable.

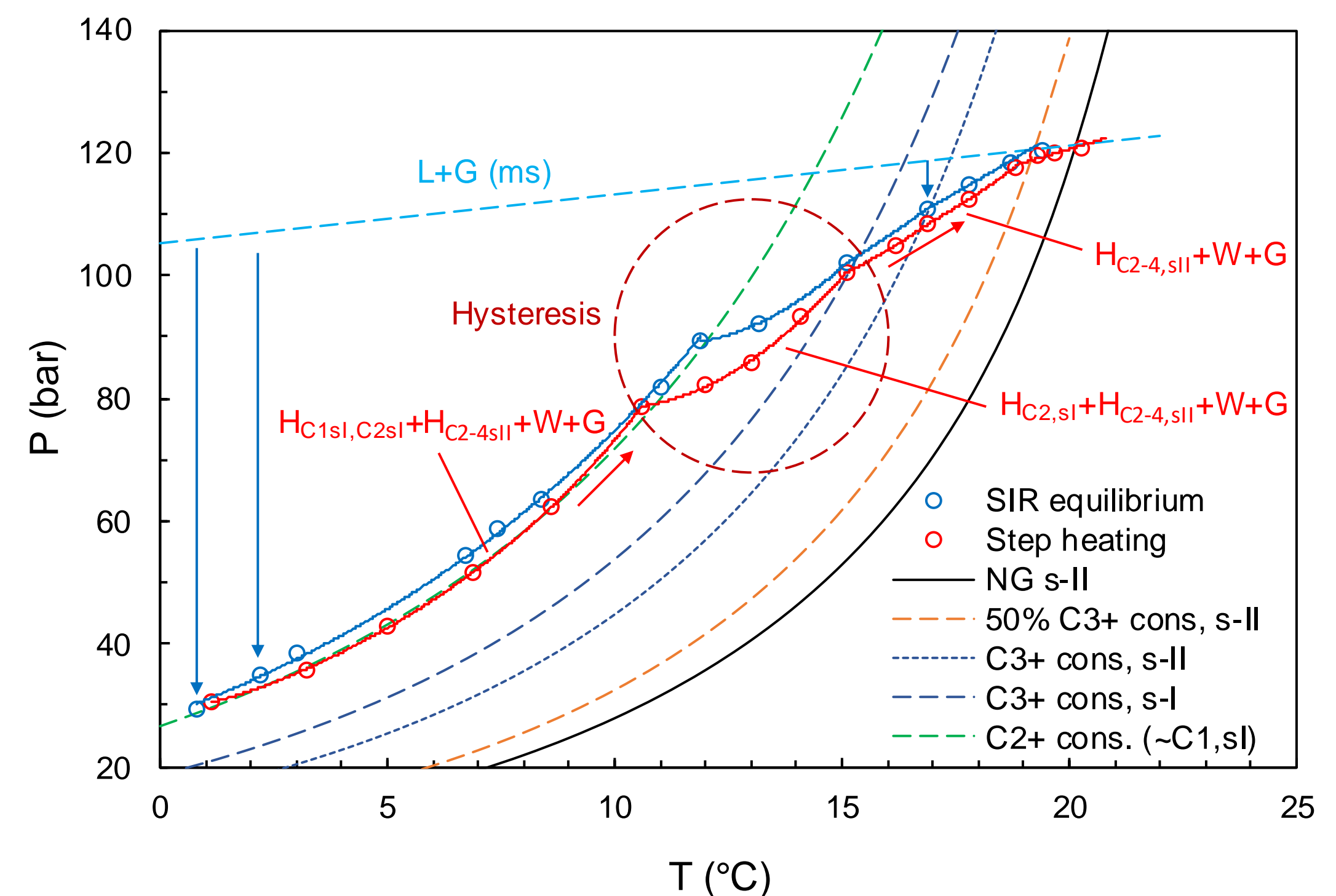


Figure 3. Experimental equilibrium data for 0.88 C₁ NG vs predicted phase boundaries for the various structures that may be present. The most stable hydrate is a C₃+ rich s-II (H_{C₃-4,s-II}). As ΔT increases, it is predicted that C₃+C₄ then C₂ are consumed in turn. Modelling the effect of this (component subtraction) predicts significant change from s-II to s-I (C₂ then C₁ large cage stabilised), which is supported by experimental data trends (isochoric slope changes). With C₂ fully consumed, an s-I C₁-rich phase (H_{C₁,sI}) becomes stable at the highest ΔT , where it comprises most of the hydrate present.

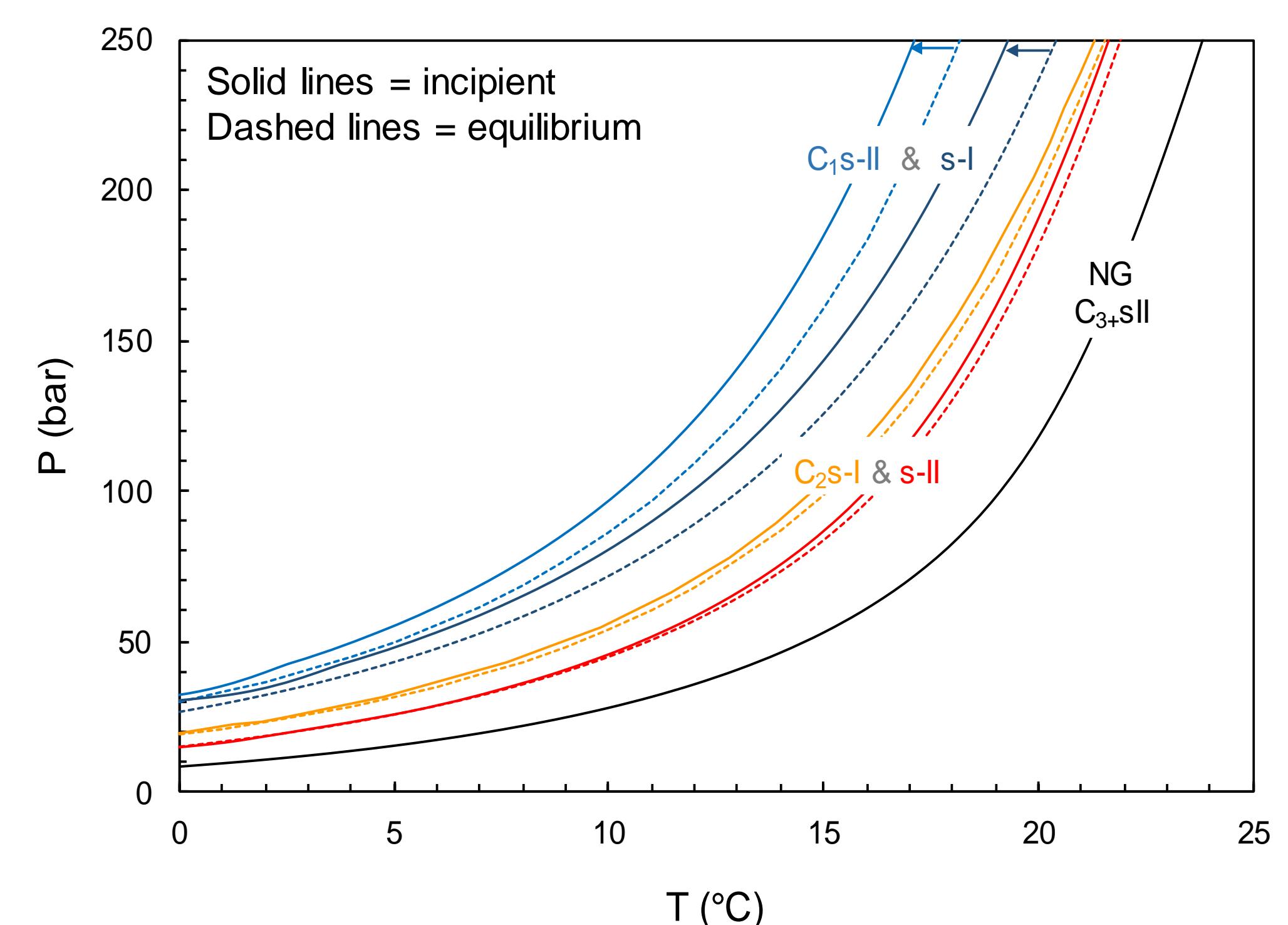


Figure 4. Novel MultiHSZ model predicted 'incipient' phase boundaries vs. equilibrium for the NG in Figure 3. 'Incipient' is for structures that could form (e.g. C₁ s-I) assuming no hydrate present so gas is of initial composition (metastable L+G). 'Equilibrium' (component subtraction approach) is for where consumption of components (e.g. C₂₋₄) / fractionation reduces dilution effects (on fugacities), increasing stability of hydrate phases for remaining formers.