Ostwald's step rule: a consequence of growth kinetics and nano-scale energy landscape

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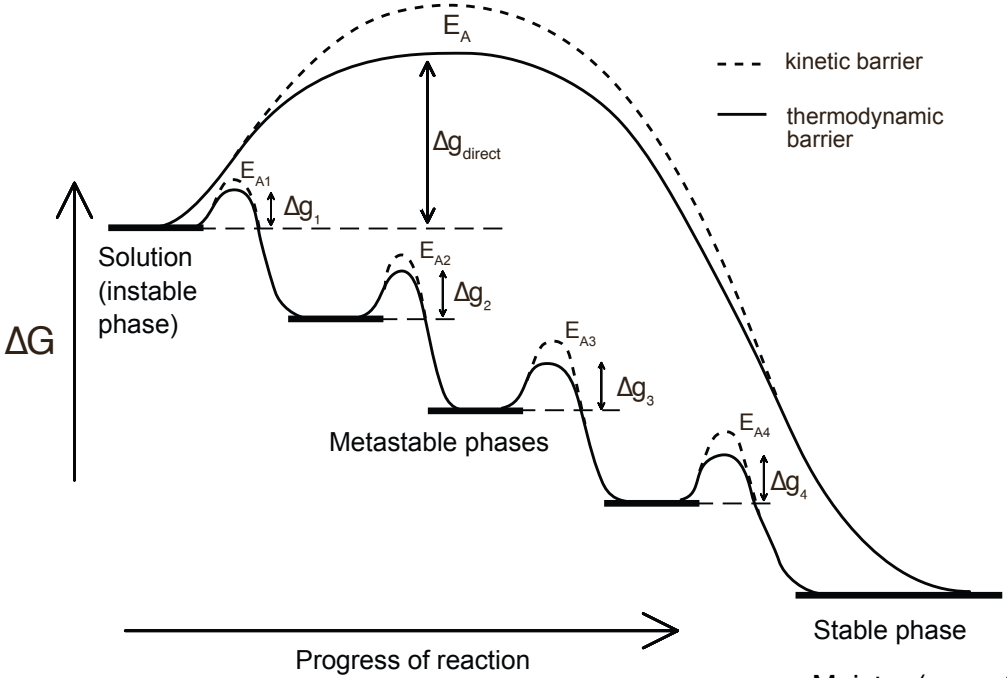

Meister (accepted, IAS Special Publications)

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In his 1897, Friedrich Wilhelm Ostwald described the phenomenon that hydrous sodium chlorate precipitates from an oversaturated solution, despite that this phase is more soluble than the non-hydrous salt. This phenomenon is commonly referred to as Ostwald's step rule (e.g. Morse & Casey, 1988), and it is interpreted such that **not the thermodynamically most stable phase but a metastable phase is formed first**.

Friedrich Wilhelm Ostwald
1853-1932

Ostwald, W. (1897) *Studien über die Bildung und Umwandlung fester Körper. 1. Abhandlung: Übersättigung und Überkaltung*.
In: Zeitschrift für Physikalische Chemie (International Journal of Research in Physical Chemistry and Chemical Physics) 22, 289–330.

However, Ostwald did not mention the word “metastable“.

The original german text says that the phase which is “nächstliegend“ (i.e. “nearest“) forms first:

“… Solche Erscheinungen treten auch beim Schmelzen und Verdichten von Dämpfen, ja sogar bei homogenen chemischen Reaktionen überaus häufig auf, und ich möchte die Gesamtheit der bisherigen Erfahrungen über den Gegenstand in den allgemeinen Satz zusammenfassen, dass beim Verlassen irgend eines Zustandes und dem Übergang in einen stabileren ***nicht*** *der unter den vorhandenen Verhältnissen* ***stabilste*** *aufgesucht wird, sondern der* ***nächstliegende****.“*

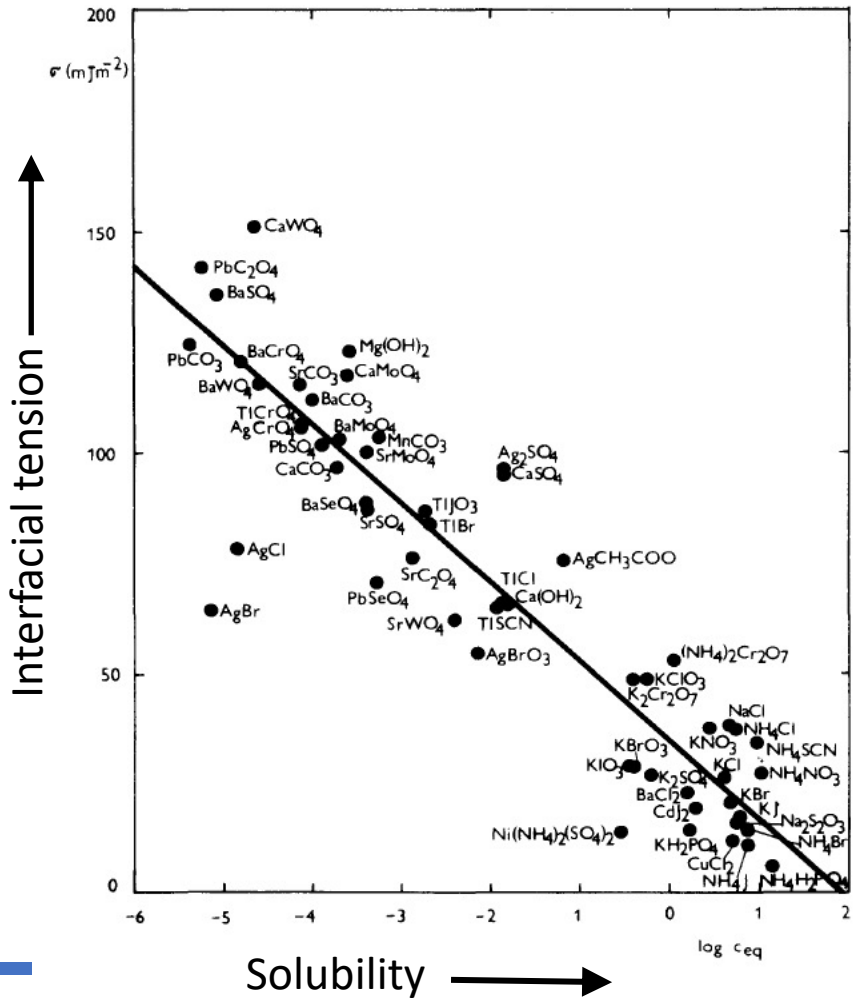
“… Such phenomena also frequently occur during melting and condensation of steam and even in homogeneous chemical reactions, and I would like to summarize the previous experiences with this matter in the single phrase that during departure from any state, and the transition to a more stable one, ***not*** *the under given circumstances* ***most stable state*** *is reached, but* ***the nearest one****.“*

Friedrich Wilhelm Ostwald 1897

Söhnel (1982) described the general relation that phases with a higher solubility have a lower interfacial tension

→ The metastable phases are more “similar“ or “nearer“ to the aqueous phase.

This relationship could explain Ostwald‘s step rule. However there are exceptions.



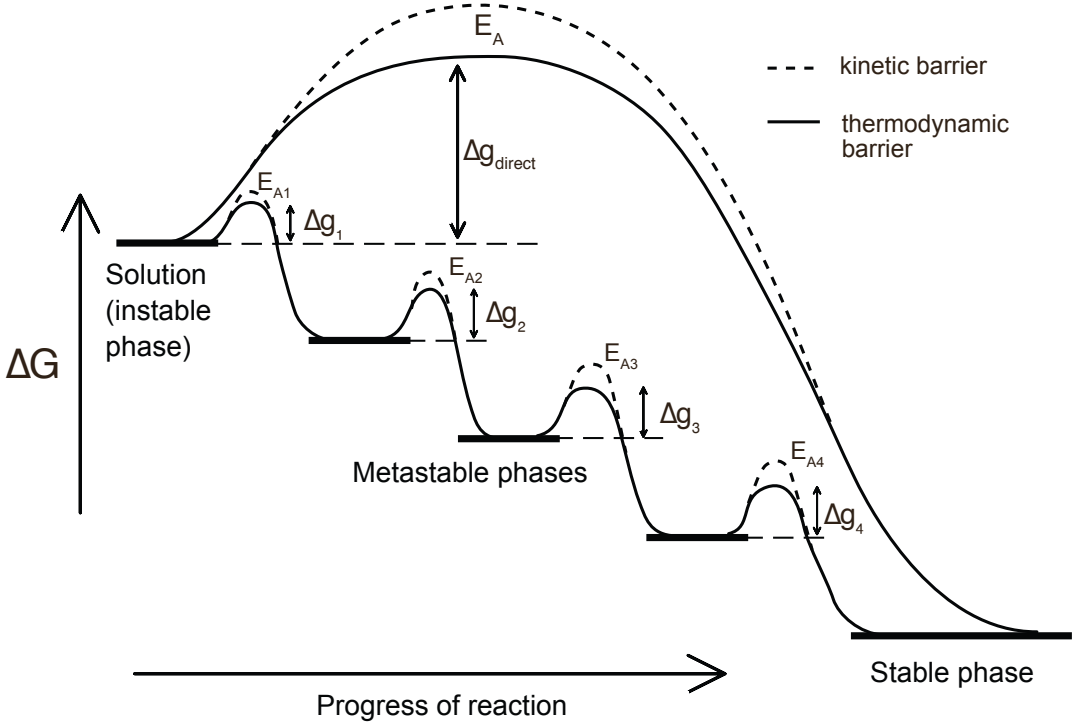
SÖHNEL, O. (1982) Electrolyte crystal-aqueous solution interfacial tensions from crystallization data. *J. Crystal Growth* **57**, 101–108.

Alternatively, we may define “nächstliegend“ as the phase that has the **lowest kinetic barrier**. In this way, Ostwald‘s step rule would be always valid.

With this definition, Ostwald‘s step rule would become equivalent to the Arrhenius equation:

$$k = A \cdot e^{-\frac{E_A}{RT}}$$

k = kinetic constant
A = pre-exponential factor
EA = activation energy
R = gas constant
T = temperature



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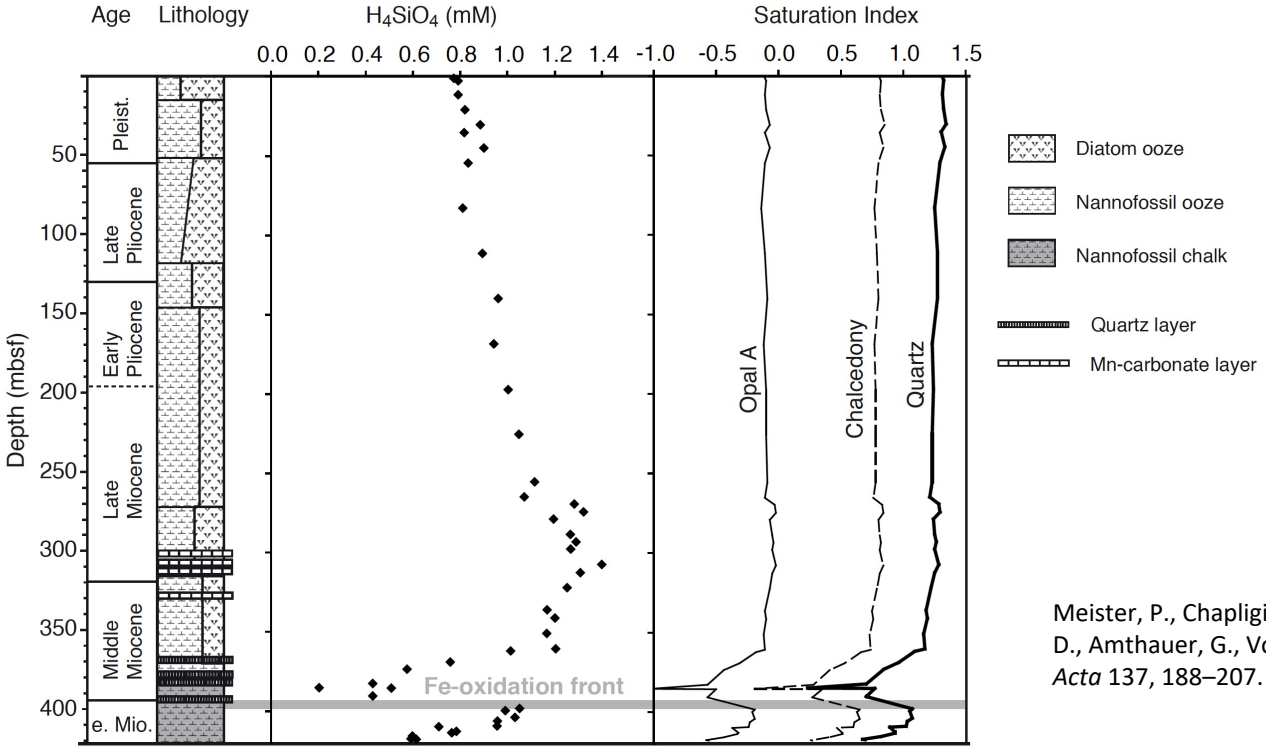
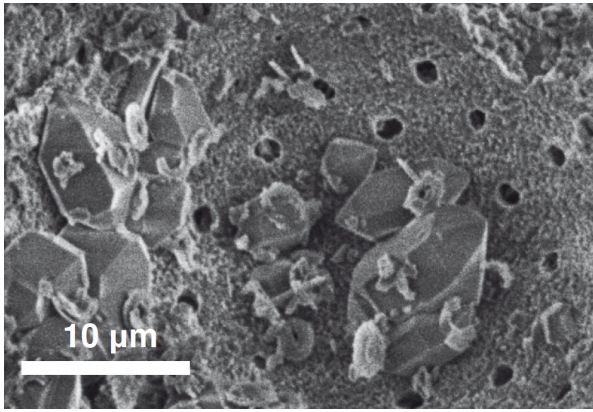
⇒ At the nano-scale, energy barriers are decicive for the molecular pathway of mineral growth (e.g. by attachment of nanoparticles).

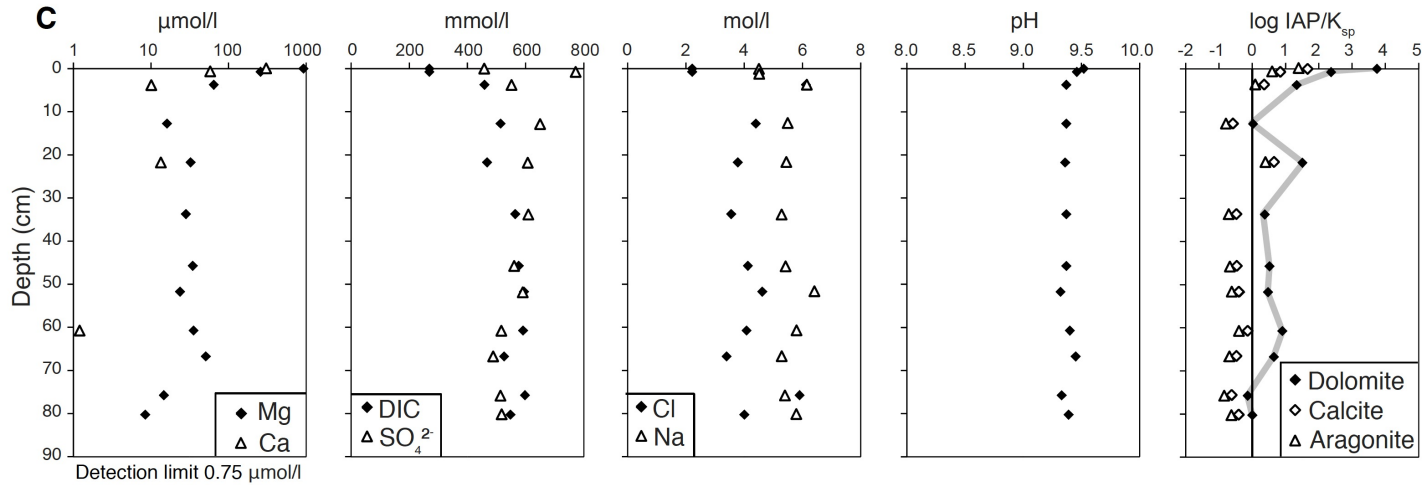
As an example we may look at opal to quartz transformation at IODP Site 1226: Quartz is supersaturated due to opal dissolution, but it is kinetically inhibited as long as the metastable phase remains saturated. Only at 400 mbsf, opal-A is undersaturated and quartz forms.





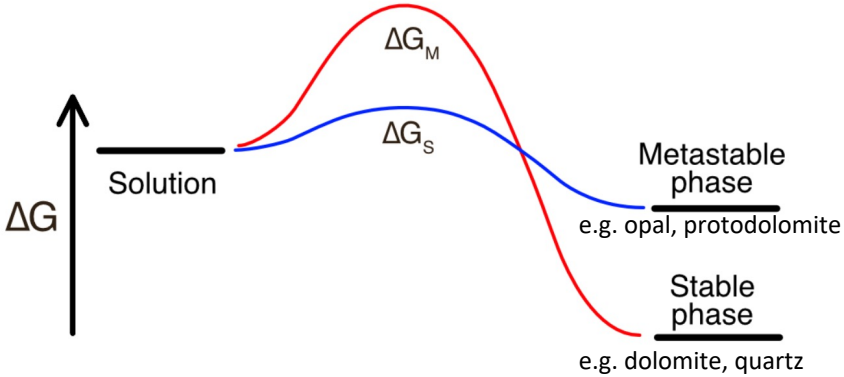
Meister, P., Chapligin, B., Picard, A., Meyer, H., Fischer, C., Rettenwander, D., Amthauer, G., Vogt, C., and Aiello, I.W. (2014) *Geochim. Cosmochim. Acta* 137, 188–207. https://doi.org/10.1016/j.gca.2014.03.035

Dolomite formation would be largely inhibited due to supersaturation of metastable phases, but may form under fluctuating conditions in the surface water.

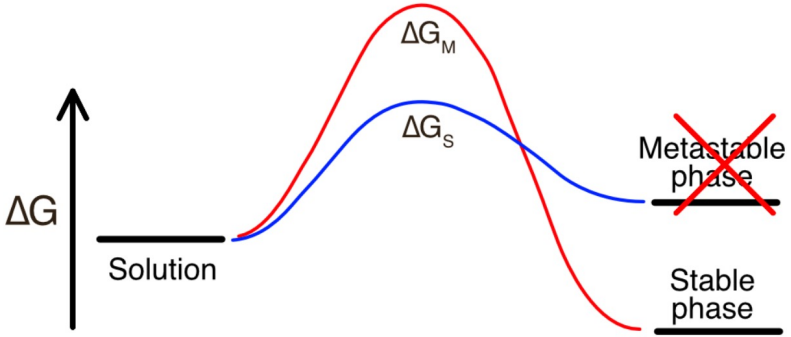


Meister, P., Reyes, C., Beaumont, W., Rincon, M., Collins, L., Berelson, W., Stott, L., Corsetti, F., and Nealson, K.H. (2011) *Sedimentology* 58, 1810–1830. https://doi.org/10.1111/j.1365-3091.2011.01240.x

Both phases supersaturated



Only stable phase supersaturated



Meister, P. Ostwald's step rule: a consequence of growth kinetics and nano-scale energy landscape. Accepted in: "Nucleation and growth of sedimentary minerals", Eds. P. Meister, C. Fischer, and N. Preto, IAS Special Publications.

Conclusions

- Ostwald‘s step rule can be better phrased as:
  “The phase with the lower kinetic barrier forms first.“
- In this wording, Ostwald‘s step rule would become equivalent to the Arrhenius equation and should be always valid.
- The presence/supersaturation of a metastable phase can prevent the formation of a more stable phase. Even if the mechanism is still not entirely clear, this effect may in particular have a major control on diagenetic processes.
- One consequence of Ostwald‘s step rule is that alternative, nanoparticular (i.e. non-classical) pathways may become more competitive.