The choice of a thermodynamic formulation dramatically affects modelled chemical zoning in minerals

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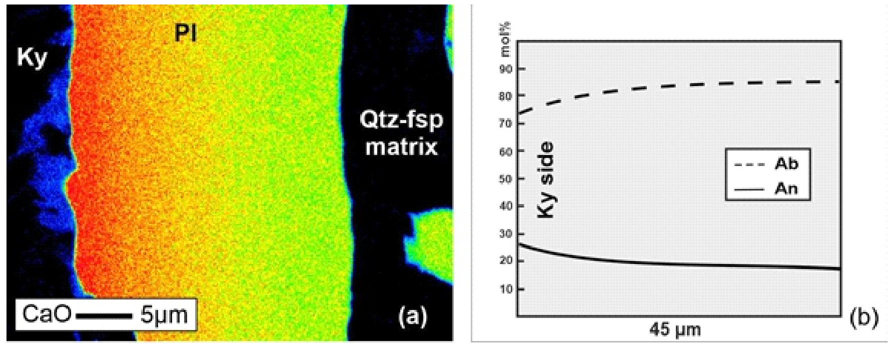
Motivation

In petrology, several thermodynamic approaches have been suggested to quantify systems under chemical and mechanical gradients (e.g. Powell et al., 2018; Tajčmanová et al., 2014;2015). Yet, their thermodynamic admissibility has not been investigated in detail. Here, we focus on a fundamental question: which thermodynamic formulation for petrological systems under gradients is appropriate – mass or molar?

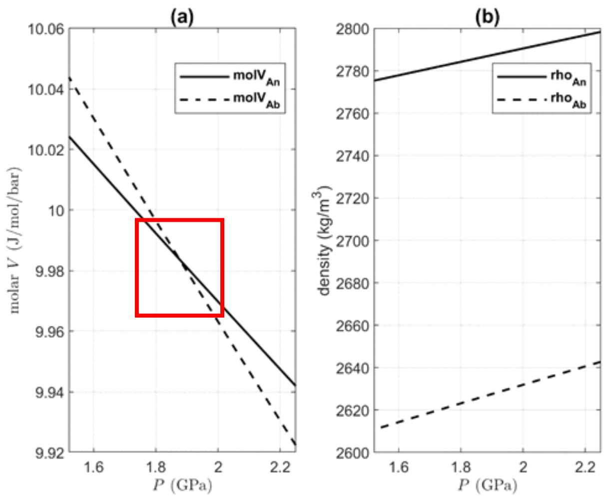
In the absence of a specific experiment which would prove the correct thermodynamic solution, the entropy production principle is the only way how to evaluate the admissibility. Therefore, we provide a comparison of both thermodynamic formulations for chemical diffusion flux, applying the positive entropy production principle as a necessary admissibility condition.

Test example



An example of a chemically-zoned plagioclase grain. a) The element distribution map where the color-coding corresponds to the variation in CaO. b) Representative compositional profile (line scan) across the plagioclase grain. Pl = plagioclase, Ky = kyanite, Qtz = quartz, fsp = feldspar, Ab = albite, An = anorthite.

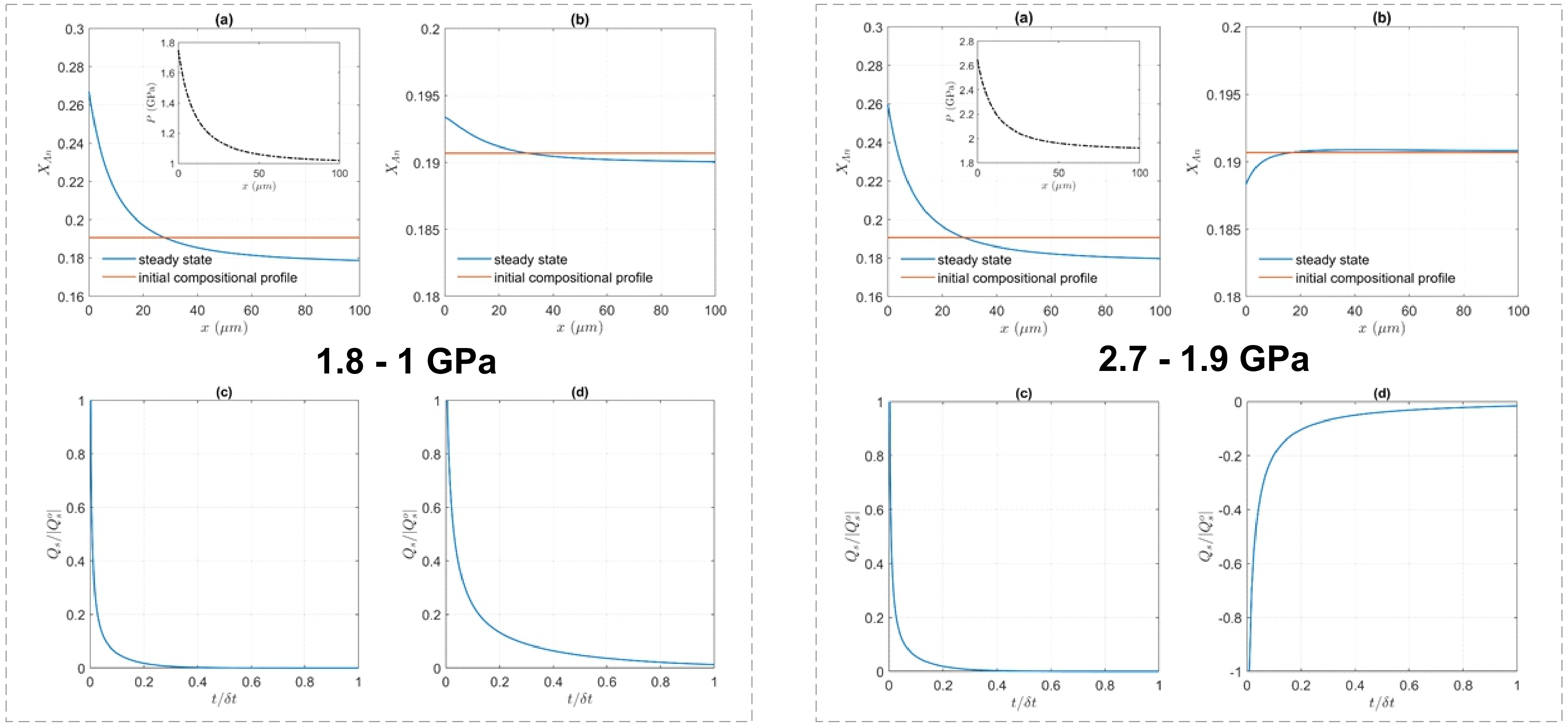
Molar volume vs. density changes with pressure



a) Molar volumes (J/mol/bar) and b) density (kg/m3) of albite and anortite endmembers as a function of pressure (P).

Pressure corresponding to the crossing in the red rectangle in a) was used as a threshold for exploring the evolution of compositional profile and the trend of entropy production on the way to equilibrium.

Mass vs. moles on the way to equilibrium: how does entropy behave?



Resulting compositional profile (X Anorthite = Ca/(Ca+Na)) as a funcion of distance for a) mass and b) molar solution for two pressure profiles assumed (1.8 - 1 GPa left and 2.7-1.9 GPa right) are shown (pressure profile as inset in a)). Evolution of entropy production with time (both normalized) for the same pressure variation using the diffusion flux in c) Mass (following the approach of Tajčmanová et al. 2015) and d) Moles (as suggested by Powell et al., 2018).

Under this pressure gradient, the diffusion process leads to the development of a chemical zoning on the way to equilibrium. The final compositional profile at given time in this model corresponds to the steady state. Under these conditions the diffusion flux is zero but the plagioclase grain is chemically zoned.

Left: (a,b) The trend of chemical zoning is similar for both, whereas the magnitude is about one order of magnitude different. (c,d) The trend of the entropy production is for both, mass and molar solution, positive, i.e. both solutions are apparently admissible. However, such a difference in prediction of the chemical zoning would be critical for a correct application of petrological approaches and interpretations. I.e. only one of these two solutions can correctly predict the natural observations. ***The question now is, which of the two is correct?***

Right: (a,b) The molar trend of the chemical zoning above the 1.88 GPa threshold is completely opposite than the chemical trend inferred from the mass formulation. (c,d) Entropy production is positive for the flux formulation in mass and negative for the molar solution. ***The negative entropy production does not fulfill the thermodynamic admissibility.***

Conclusions and future investigations

The direct documentation of stress/pressure variations in rock samples via elastic barometry, HR-EBSD and X-ray microdiffraction has become very popular in geosciences. This augmented the need to appropriately quantify the complex chemo-mechanical processes in rock systems.

We show that the inappropriate solution has dramatic consequences for understanding the key processes in petrology, such as chemical diffusion in the presence of stress gradients. It can lead to a completely opposite chemical zoning.The example here is for plagioclase- the most abundant mineral in the Earth's crust. Similar flip in molar volume also exists for grossular-pyrop end members in garnet - the most popular mineral in metamorphic petrology.

The simple molar formulation (e.g. as suggested by Powell et al. 2018) for systems under pressure gradients is thermodynamically inconsistent. An admissible molar equivalent for such systems is not excluded. However, any attempt requires a rigorous demonstration of the thermodynamic admissibility.

References:
Powell et al (2018) On equilibrium in non-hydrostatic metamorphic systems. JMG, 36, 419–438 ; **Tajčmanová et al., (2014)** Grain-scale pressure variations and chemical equilibrium in high-grade metamorphic rocks. JMG 32, 195–207. ; **Tajčmanová et al., (2015)**Grain-scale Pressure Variations in Metamorphic Rocks: Implications for the Interpretation of Petrographic Observations. Lithos 216-217, 338-351.