

## Introduction

For an ongoing project to study the transport processes within a volcanic conduit, including crystallization and degassing, we are coupling a **thermodynamics** model (TD) to a **computational fluid dynamics** (CFD) model allowing for a fully thermo- and fluid dynamically **consistent** simulation.

Despite the wide range of TD model families available, e.g. MELTS (Ghiorso and Sack, 1995), THERMOCALC (Holland and Powell, 2011), PERPLE\_X (Connolly, 2005), the need to re-implement a TD model to suit our cause is become apparent for the reasons stated below. Here, we can only give a short account of our approach to one of the problems encountered: **The characterization of miscibility gaps.**

## Why re-invent the wheel?

Given all the established thermodynamics software and toolboxes, we still decided to endeavour re-implementing one of them for two reasons:

### ► Ensuring computing performance

The interface between separate TD and CFD programs forms a severe bottleneck. Direct integration and compilation of TD into the CFD code is necessary for acceptable run-times.

### ► Learning how to use TD model properly

Using a complex TD model requires knowledge of its range of applicability to stay within it, or to know when it is safe to transgress those limits (e.g. a mixing-model being valid for what bulk compositions). This information is often not obvious at first glance.

On gaining more insight, a third requirement was added to the list and soon became paramount:

### ► Ensuring numerical consistency

Fully coupling a TD and a CFD model creates a feedback loop where the output of one model at one time-step is the other's input at the next and vice versa. This amplifies inconsistencies resulting solely from the *numerical* implementation of a *physically* consistent TD model that would be insignificant under normal operation.

## The thermodynamics model

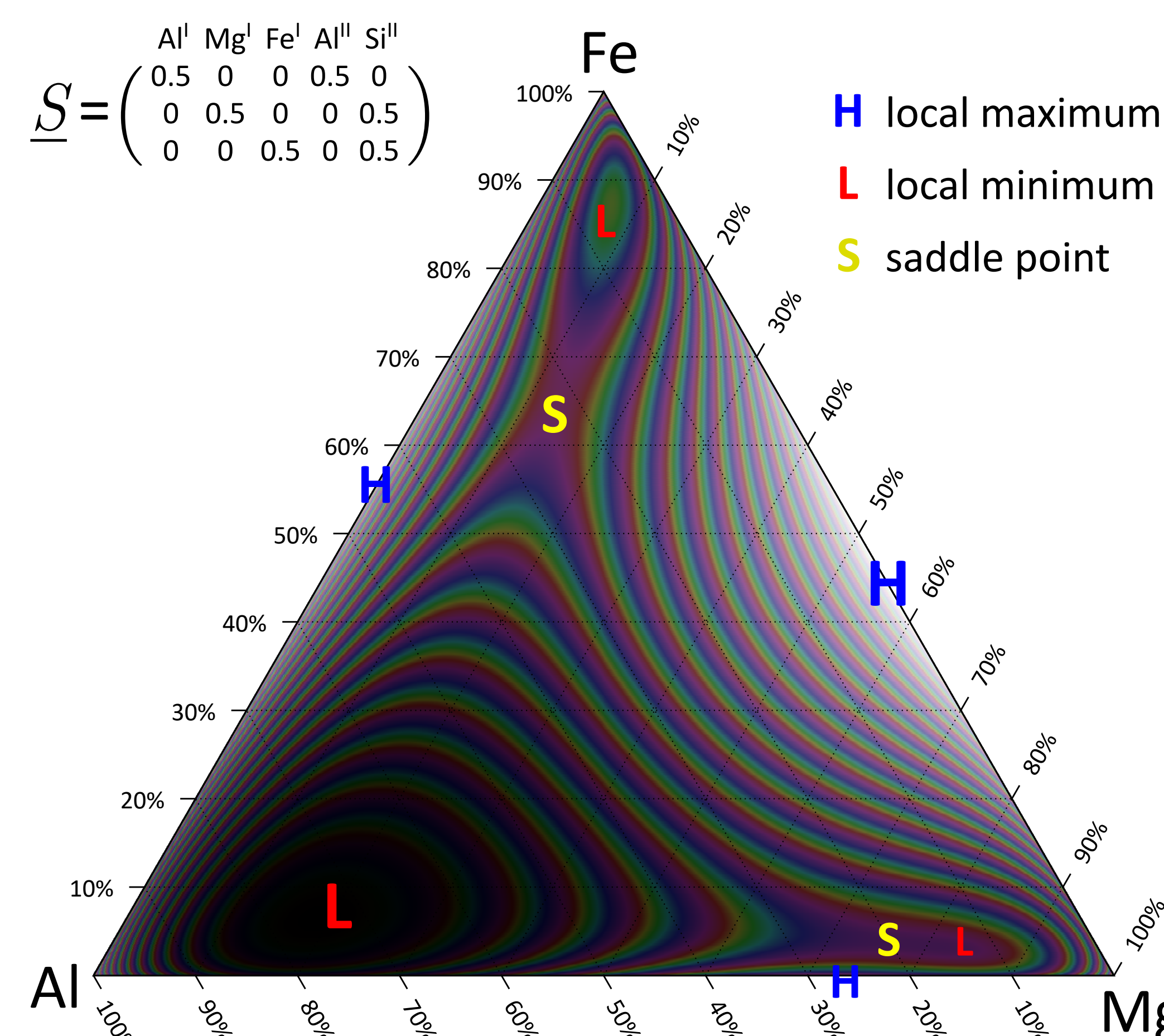
TD models solve a system's **equation of state (EOS)** given as a thermodynamic potential, e.g. the Gibbs free energy  $G$ , at a given state (pressure, temperature, bulk composition,  $PTX$ ) under the assumption of equilibrium for the stable phase composition. They consist of three parts that are, at least in principle, independent from each other:

- The so-called **database**, i.e. the EOSs of the pure end-member phases,
- the **mixing models** (also activity-composition) of how the singles phases interact, and
- a **solver** to find the composition at equilibrium under given  $PTX$  conditions.

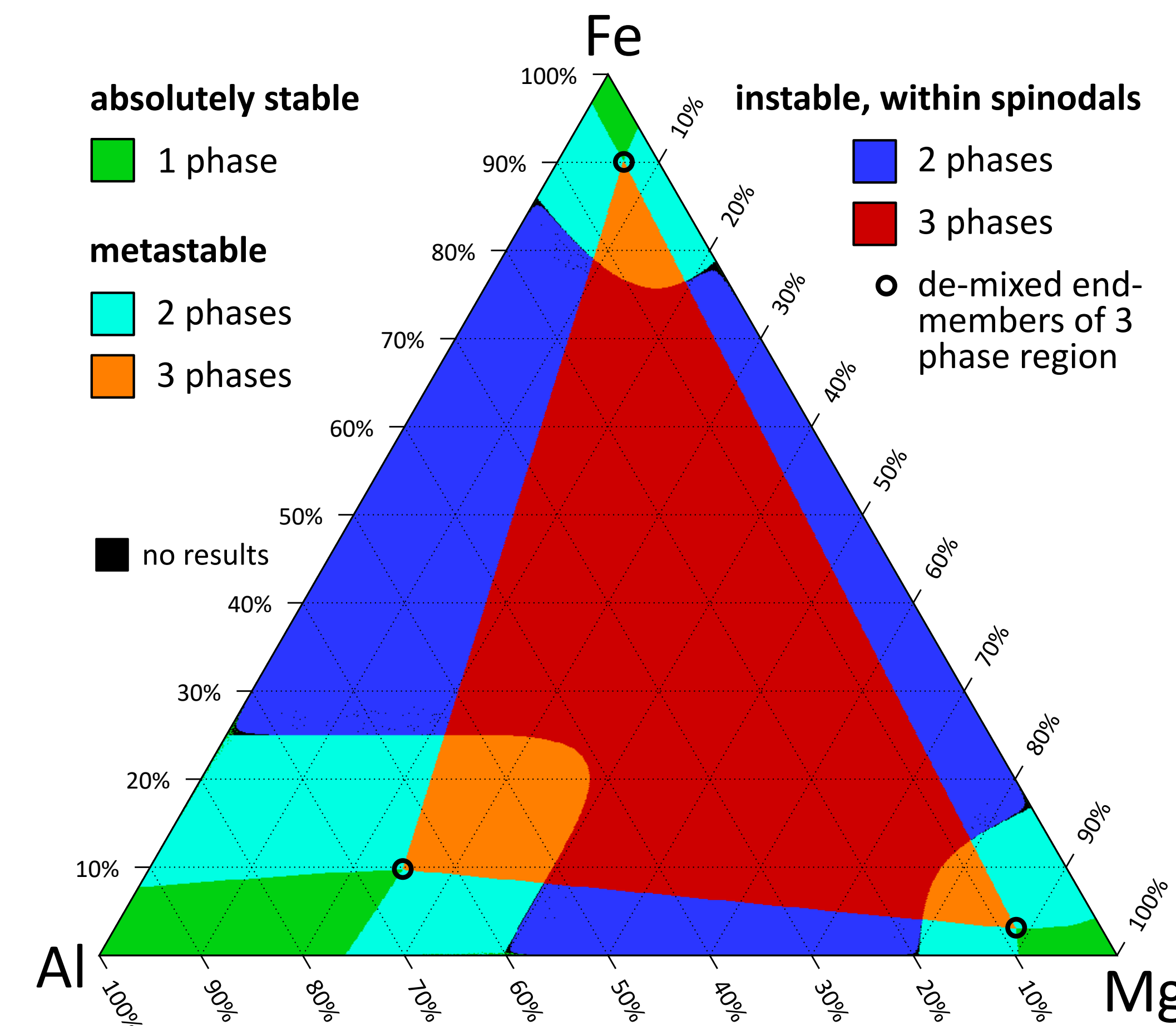
We chose to re-implement the TD model of Holland and Powell (2011) using their database and mixing models but writing a new solver in Fortran to be compatible with our CFD program (Flow3D).

**Figure 1:** Topography of the Gibbs energy of mixing  $G_{\text{mix}}$  (eq. 1, on the right) for a fictive ternary system  $\text{Al}^{\text{I}}\text{Al}^{\text{II}}\text{O}_3$ ,  $\text{Mg}^{\text{I}}\text{Si}^{\text{II}}\text{O}_3$ ,  $\text{Fe}^{\text{I}}\text{Si}^{\text{II}}\text{O}_3$  with mixing on two but indistinguishable sites. It shows three local maxima, already suggesting miscibility gaps, and three local minima close to the three end-members.

Parameters:  $T = 1474 \text{ K}$ ;  $G_i = 0$ ,  $\delta G_i = 8.495$ ,  $W_{\text{AM}} = 8$ ,  $W_{\text{AF}} = 6$ ,  $W_{\text{MF}} = 4 \text{ kJ/mol}$ ;  $a_i = [1.0, 1.1, 1.4]$ , and



**Figure 2:** Miscibility landscape. (see text on the right)



## The mixing model

The full expression for the Gibbs energy of mixing  $G_{\text{mix}}$  of an  $n$ -phase system based on the Holland and Powell (2011) system is:

$$G_{\text{mix}} = \sum_{i=1}^n x_i \left( G_i + \delta G_i + R T \ln \prod_{j=1}^{n_s} \left( \sum_{k=1}^n S_{jk} x_k \right)^{S_{ji}} \right) + \underbrace{\sum_{k=1}^n \frac{2}{a_k x_k} \sum_{i=1}^{n-1} \sum_{j>i}^n x_i x_j \frac{a_i a_j}{a_i + a_j} W_{ij}}_{\text{NIM}} \quad (1)$$

$x_i$  is the normalized ( $\sum x_i = 1$ ,  $x_i \geq 0$ ) molar amount of phase  $i$ , and  $G_i$  its pure end-member Gibbs energy.  $\delta G_i$  summarizes all constant corrections to this while in mixture. Also any parameter may depend on pressure  $P$  and temperature  $T$ .  $R$  is the gas constant.

**Ideal mixing on sites (IMOS)** is described by an  $n_s \times n$  matrix  $\underline{S}$ , where  $S_{ji} \geq 0$  is the site occupancy of site  $j$  by end-member  $i$ .

**Non-ideal mixing (NIM)** is described within the asymmetric formalism (Holland and Powell, 2003) by asymmetry parameters  $a_i \geq 0$  and pairwise interaction energies  $W_{ij}$  between phases  $i$  and  $j$ .

For  $\underline{S} = \underline{1}$  the identity matrix and all  $W_{ij} = 0$ , (1) reduces to the well-known simple ideal mixing equation:  $G_{\text{mix}} = \sum_{i=1}^n x_i (G_i + R T \ln x_i)$ .

## Miscibility gaps

Miscibility gaps *can* occur if, for a given composition  $\mathbf{x}$ , there is a linear composition of two or more different compositions  $\sum (b_j \mathbf{x}'_j) = \mathbf{x}$  for which  $\sum [b_j G_{\text{mix}}(\mathbf{x}'_j)] \leq G_{\text{mix}}(\mathbf{x})$ . Spontaneous de-mixing into this combination of phases *will* occur, when  $\mathbf{x}$  is within the **spinodals** of the system. Within the **binodals**, the composition is metastable.

Available TD programs deal with this by using *a priori* knowledge of the behaviour of the mixing model, limiting their applicability to cases, where such is available. We are working on a semi-analytic algorithm to characterize a mixing model in terms of its miscibility gaps.

Results for the model of Fig. 1 are shown in Fig. 2. Checking for the spinodals can be done analytically by checking the sign of the smallest eigenvalue of  $\partial^2 G_{\text{mix}}(\mathbf{x}) / \partial \mathbf{x}^2$ . As the miscibility landscape is completely determined by the second derivatives of  $G_{\text{mix}}$ , it can be transformed by linear functions without changing its character. Making  $\nabla G(\mathbf{x}) = 0$  locally that way is sufficient to determine whether  $\mathbf{x}$  lies on the lower convex hull (LCH) of  $G_{\text{mix}}$  and thus is absolutely stable. In similar fashion, up to  $n$  supports of the LCH (black circles in Fig. 2) can be found. Compositions within them are known to de-mix into those points.

Our algorithm is currently being optimized and validated, and can be expected to be published in its entirety in due course.

## References

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