Application Example:

Microsegregation during Solidification

Database(s):	**TCFE11 and MOBFE6 or newer**	Module(s):	**Diffusion Module (DICTRA)**
Version required:	**Thermo-Calc 2021b or newer**	Calculator(s):	**Scheil, Equilibrium**
Material/Application:	**Steel / Casting**		
Calculation name:	**D_08_Diffusion_Microsegregation_During_Solidification**		

INTRODUCTION

This example shows only a few of the capabilities of Thermo-Calc together with the add-on Diffusion Module (DICTRA) to investigate and predict microsegregation (solute redistribution) during solidification.

It is based on a real case where the elemental distribution of a continuously cast steel was measured revealing the concentration of the elements Si, Mn, and P as shown in Figure 1. The profile results from the well-known segregation across secondary dendrite arms. The interesting point is that the elements Si and Mn show the expected positive segregation (higher concentrations) in the interdendritic regions. The peak of the P content, on the other hand, is shifted compared to Si and Mn, and, in fact, shows negative segregation in the interdendritic region. This is unexpected and counterintuitive.

This experimental finding is explained in this example using a simplified chemistry of the investigated steel, herein referred to as "Steel C", with composition Fe - 0.8% Mn - 0.7%Si - 0.03%P - 0.4%C. The simplification of the real steel chemistry is made to make the calculations fast and the results easier to interpret. Similar calculations can of course also be performed for more complete chemistries and for far higher alloyed special steels or stainless steels. All calculations can be reproduced using the steels database TCFE11 or newer together with the mobility database MOBFE6 or newer.

The example also touches on some very basic concepts for metallurgy and using Thermo-Calc, such as stable and meta-stable phase diagrams, Scheil and para- or partial-equilibrium Scheil solidification simulations.

The calculations are based on ones performed in the frame of a research project funded by the European Union called VESPISM – Virtual Experiments to Solve Problems in Metallurgy – conducted from 2001 to 2004 (https://cordis.europa.eu/project/rcn/55407_en.html).
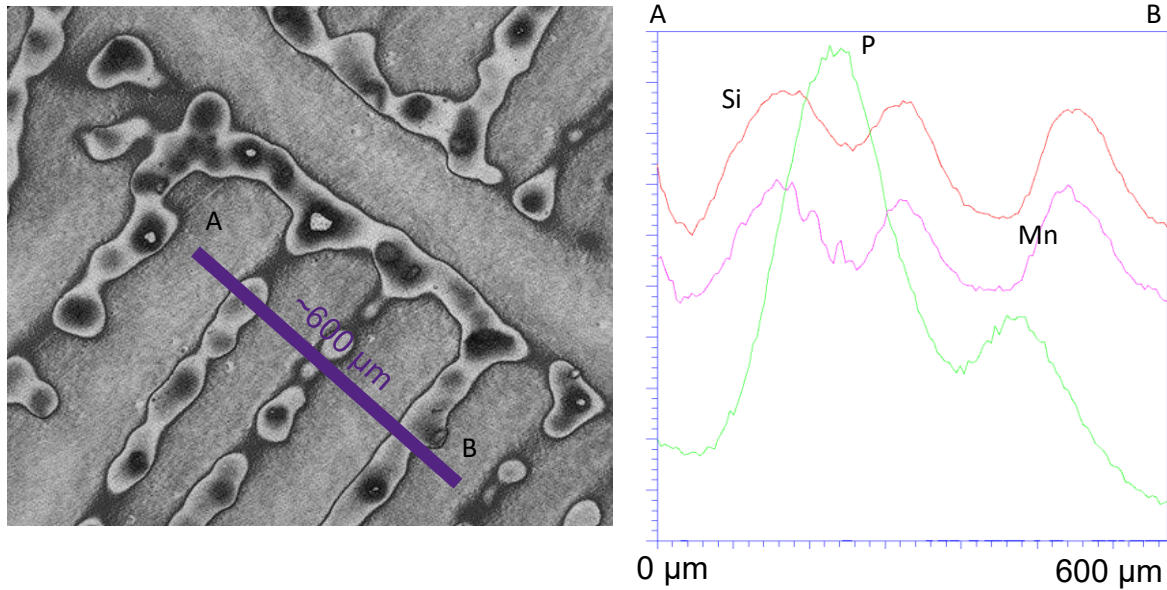
Figure 1. Micrograph of solidification microstructure (left, for reference only) and measured element concentrations across secondary dendrite arms in continuously cast steel.

How to Run the Calculation

If you have a license for Thermo-Calc 2021b or newer, as well as the products and databases listed below, you can follow along with this example in your software. Otherwise, you can read the PDF, which discusses the materials challenges and how Thermo-Calc can be used to solve them.

To run this example, open Thermo-Calc and navigate to the Help Menu → Example Files… → Diffusion Module – DICTRA. This example includes one example file:

- **D_08_Diffusion_Microsegregation_During_Solidification:** requires a license for Thermo-Calc 2021b or newer, the Diffusion Module (DICTRA), and the Steel and Fe-alloys Databases TCFE11 and MOBFE6 or newer.

See additional in-depth Application Examples available on our website.

EXAMPLE CALCULATIONS AND EXPLANATIONS

Phase Diagram and Equilibrium Phase Fractions

Equilibrium phase diagrams show the most stable phase assemblages. They are of central importance for most metallurgical problems and are the first thing to investigate before any problem is tackled. They can be considered as maps showing single phases or combinations of phases that have the lowest possible Gibbs energy. However, attention must be paid to the fact that it is not always the most stable phase that will appear. In the Fe-C system, the most stable carbon phase is graphite, but this phase will not precipitate due to kinetic reasons. The next most stable phase is diamond, but, unfortunately, we also don't see this phase appearing. The phase that actually precipitates is cementite, Fe_3C. This means that the Fe – C phase diagram that is relevant for steel research is actually not the stable Fe – C diagram, but the meta-stable Fe – Fe_3C diagram, which can easily be calculated with Thermo-Calc by suspending the phases that will not form, in this case graphite and diamond. To investigate the solidification of "Steel C" we calculate the stable Fe – C phase diagram (dashed lines) and the meta-stable Fe-Fe_3C diagrams with 0.8% Mn, 0.7% Si and 0.03% P (Figure 2). The first solid to form is the α-phase (BCC phase) at 1490 °C (liquidus temperature). The α phase decomposes into γ-phase (Austenite or FCC phase) by a peritectic reaction at 1480 °C. Under equilibrium solidification conditions, the last liquid disappears at the solidus temperature of 1425 °C.
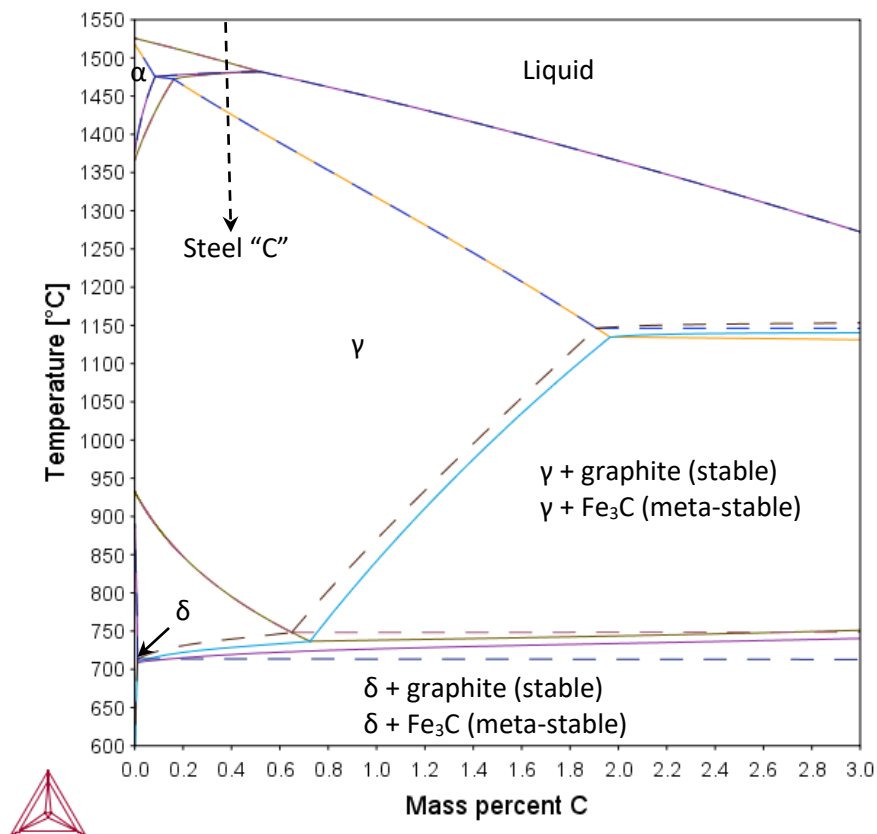

Figure 2. Stable (dashed lines) and metastable Fe - 0.8% Mn – 0.7%Si – 0.03%P – C isopleth.

Calculating the phase fractions as a function of temperature for the composition of "Steel C" (Figure 3) gives us further insight into the solidification behavior, and the primary formation of BCC followed

by the decomposition of BCC into FCC by the peritectic reaction is again seen. As the steels database (TCFE11 or newer) contains accurate volume data, the characteristic jump in volume by the peritectic reaction can be quantified, which is important for the primary solidification of the steel in the copper mould during continuous casting.
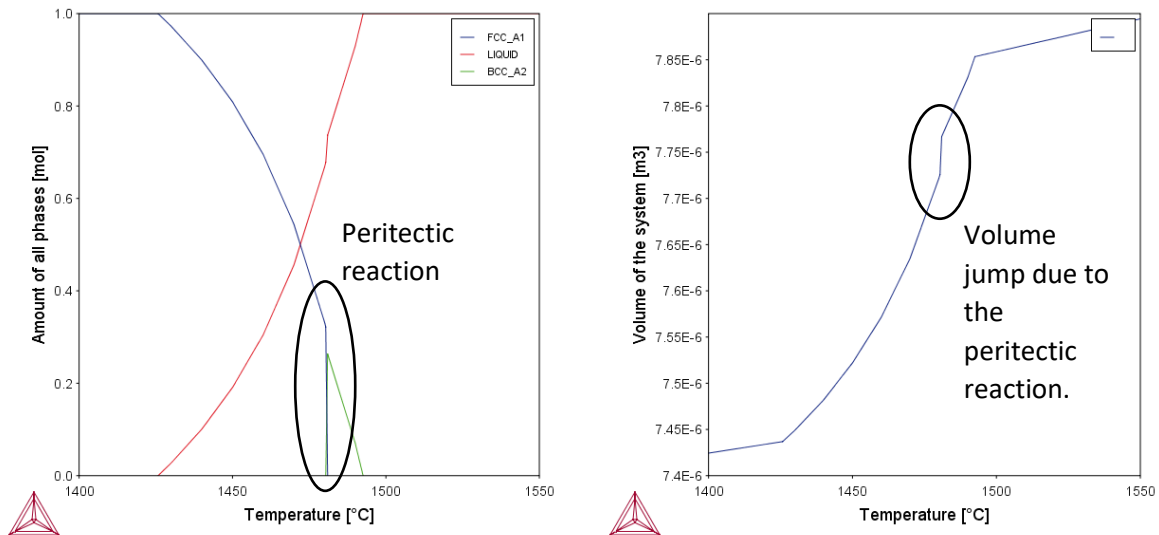

Figure 3. Phase fractions on solidification of "Steel C" with 0.8%Mn, 0.7%Si, 0.03%P and 0.4%C (right) and volume in function of temperature showing the characteristic jump in volume due to the peritectic reaction.

However, while equilibrium phase diagrams and solidification simulations give us a valuable basic understanding of the general solidification behavior, they are not fully applicable to real processes as equilibrium is never achieved in real processes. Diffusion in the solid (and in certain cases also in the liquid) is not fast enough to even out concentration gradients, and these strongly influence the solidification behavior and the phases that form. They also remain in the as-cast workpiece as segregation and can have dramatic negative effects on the performance of the final product.

Microsegregation Calculation Using the Diffusion Module (DICTRA)

Setting Up the Diffusion Problem

The Diffusion Module (DICTRA) solves for 1-dimensional diffusion problems. It assumes local equilibrium at the phase boundary and handles moving phase boundaries and the formation of new phases as they become stable. The flux is calculated using chemical potentials of all elements on either side of the phase boundary as driving force (calculated by Thermo-Calc using the TCFE database) and mobilities from the mobility database (MOBFE) under consideration of the complete diffusion matrix including all cross terms.

The calculation is set-up as shown in Figure 4 assuming a secondary dendrite arm spacing of ~200 μm. As the solidification can be assumed to proceed symmetrically, a calculation domain of 100 μm is chosen.

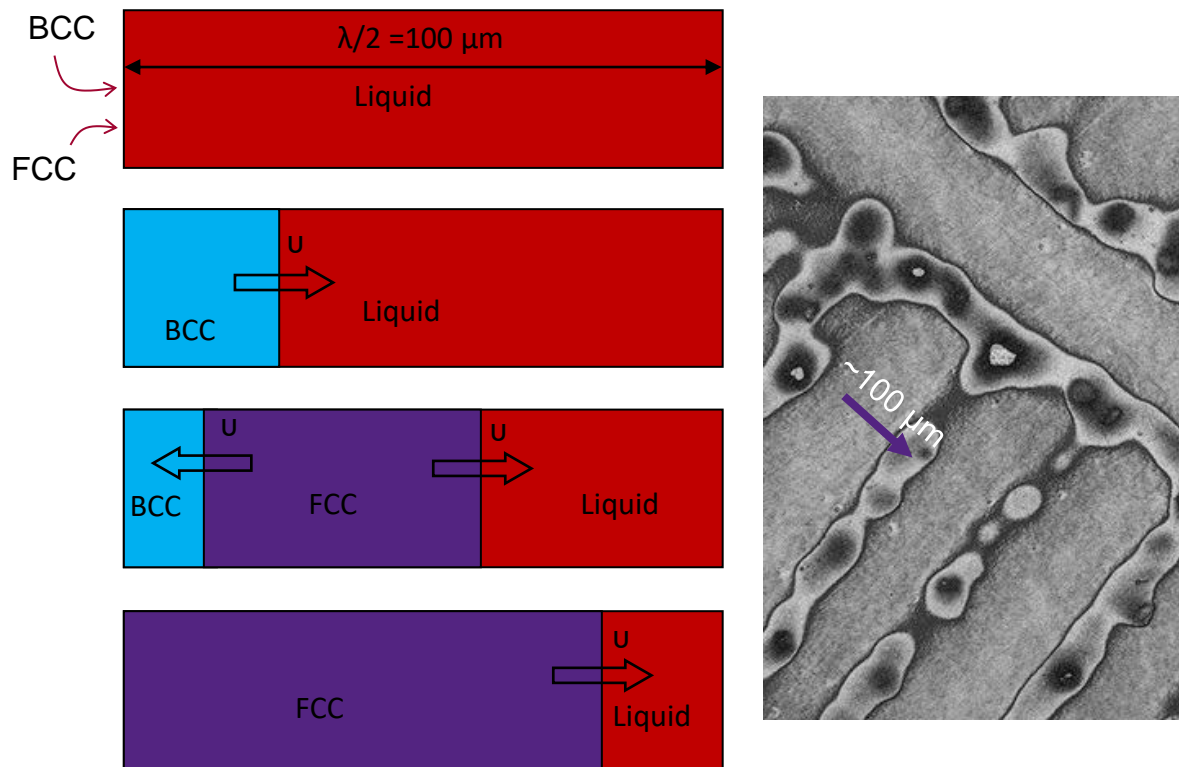*Figure 4. Set-up of the calculation domain for the Diffusion Module (DICTRA) simulation.*

A constant cooling rate of -0.2°C/sec or 600 °C in 50 minutes was chosen. This roughly corresponds to the cooling rate at about 100 mm under the surface of a medium sized continuously cast bloom. If more accurate cooling rate estimations are available, for example from a FEM solidification simulation, these can be used as input for the Diffusion Module (DICTRA) diffusion simulation. It is also possible to use enthalpy (Neumann-type boundary condition) as a boundary condition instead of temperature (Dirichlet-type boundary condition).

Interpretation of the Results of the Diffusion Calculation

Figure 5 shows the fraction solid as a function of temperature for various solidification simulations. Equilibrium solidification assumes infinitely fast diffusion of all elements in both the liquid and the solid phases. Under this assumption, the compositions of all phases follow the lines on the equilibrium phase diagram. The Classic Scheil solidification model assumes infinitely fast diffusion of all elements in the liquid and no diffusion whatsoever in the solid phases. This model is very simple and quite successful for describing certain cases. However, in cases where diffusion in the solid phases cannot be neglected, the predictions are not very accurate. For this reason, various modifications of the classic Scheil solidification model are available. Scheil with fast diffusing elements (also called partial equilibrium Scheil simulation) assumes infinitely fast diffusion of all elements in the liquid phase and one or several fast-diffusing elements in the solid phase. For steels, Carbon is set as a fast-diffusing element. Under certain situations, P, S, O, and N can also be considered as fast diffusers. Scheil with back diffusion in the primary solid phase assumes infinitely fast diffusion in the liquid and quantitatively calculates the back diffusion in the primary solid phase using a characteristic diffusion length (usually taken as half the secondary dendrite arm spacing) and the cooling rate. This Scheil model requires a mobility database. It is important to note that none of the Scheil simulations consider the solid-state phase transition BCC → FCC. For the Scheil simulation with back diffusion, this means that a choice must be made whether back diffusion should be considered in the BCC or the FCC phase. It is not possible to consider back diffusion in both phases. The obvious choice in this case is FCC, as the BCC phase disappears quite quickly and back diffusion in BCC thus has a small influence on the solidification curve. It should also be noted that for this case, the simulation with back diffusion requires choosing a temperature step < 1 °C for numerical reasons.

When calculating solidification with the Diffusion Module (DICTRA) the real diffusion of all elements in all solid and liquid phases is quantitatively considered for the actual temperature gradients. The DICTRA simulation also quantitatively describes the solid-state BCC → FCC transformation. This means that it is most likely the best approximation to the real solidification behavior. Comparing the various solidification curves reveals that the classic Scheil simulation results in an unrealistically low final solidification temperature. Scheil with fast diffusing Carbon returns more realistic results and Scheil considering back diffusion of all elements finally comes quite close to the DICTRA simulation. The difference can be attributed to the fact that BCC → FCC is not considered. In cases without such a phase transition, Scheil with back diffusion and DICTRA simulations are virtually identical. Equilibrium solidification returns the highest final solidification temperature and corresponds to solidification with an infinitively low cooling rate.
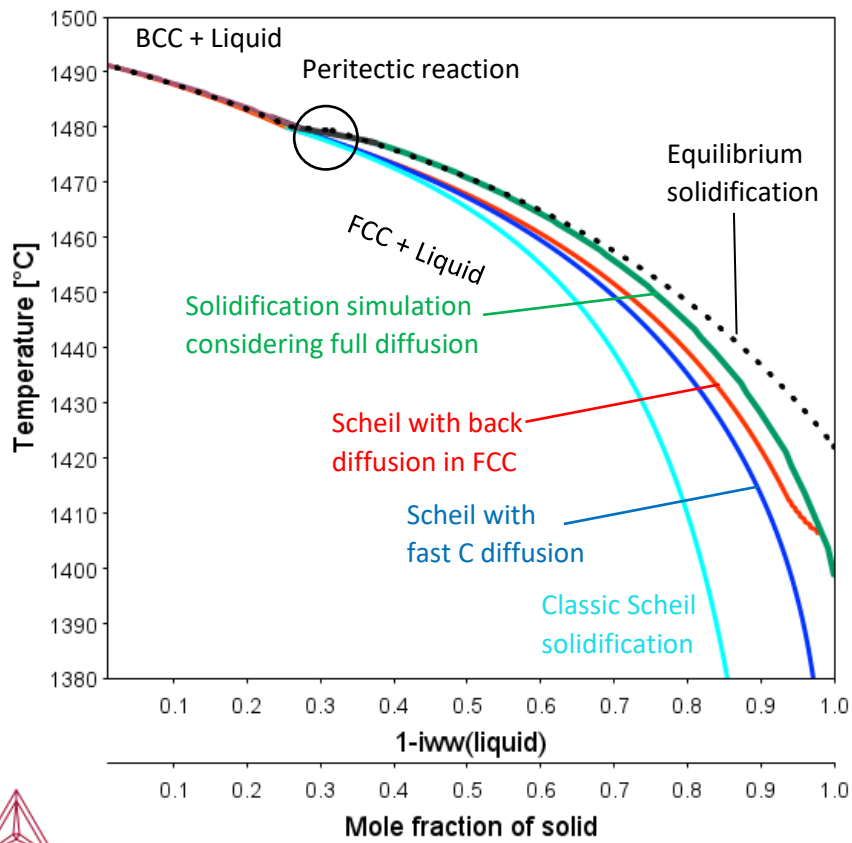
Figure 5. Calculated fraction solid as a function of temperature shown for various solidification simulations.

In Figure 6 the fractions of the solid phases (BCC and FCC) are shown as functions of time during solidification. The peritectic reaction takes about 10 seconds to complete for the chosen cooling rate.
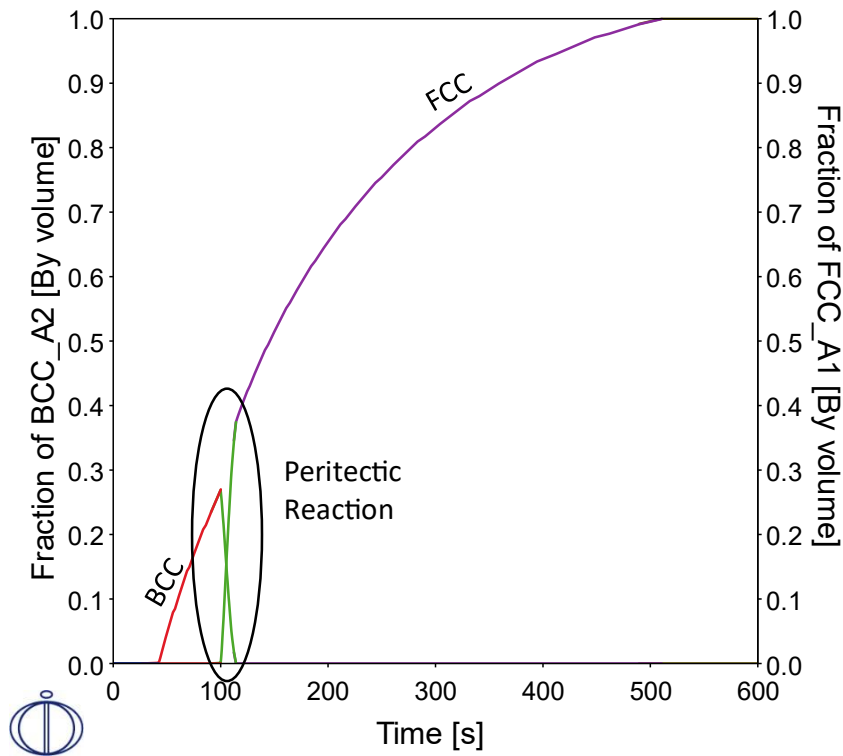

Figure 6. Fraction solid calculated for moving phase boundaries during solidification under full consideration of diffusion in all solid and liquid phases.

The concentrations of all elements during solidification are shown in Figure 7. The diffusion of carbon is so quick that already during solidification virtually no concentration gradients are found in the solid phase. This shows that a para-equilibrium Scheil solidification simulation with C defined as an infinitely fast diffusing element is a reasonable model for the simulation of solidification of steels. The diffusion of Mn and Si, on the other hand, is so slow that only insignificant diffusion occurs during solidification. P is somewhere in between C and Mn, Si and cannot be properly treated using the simple Scheil solidification model.
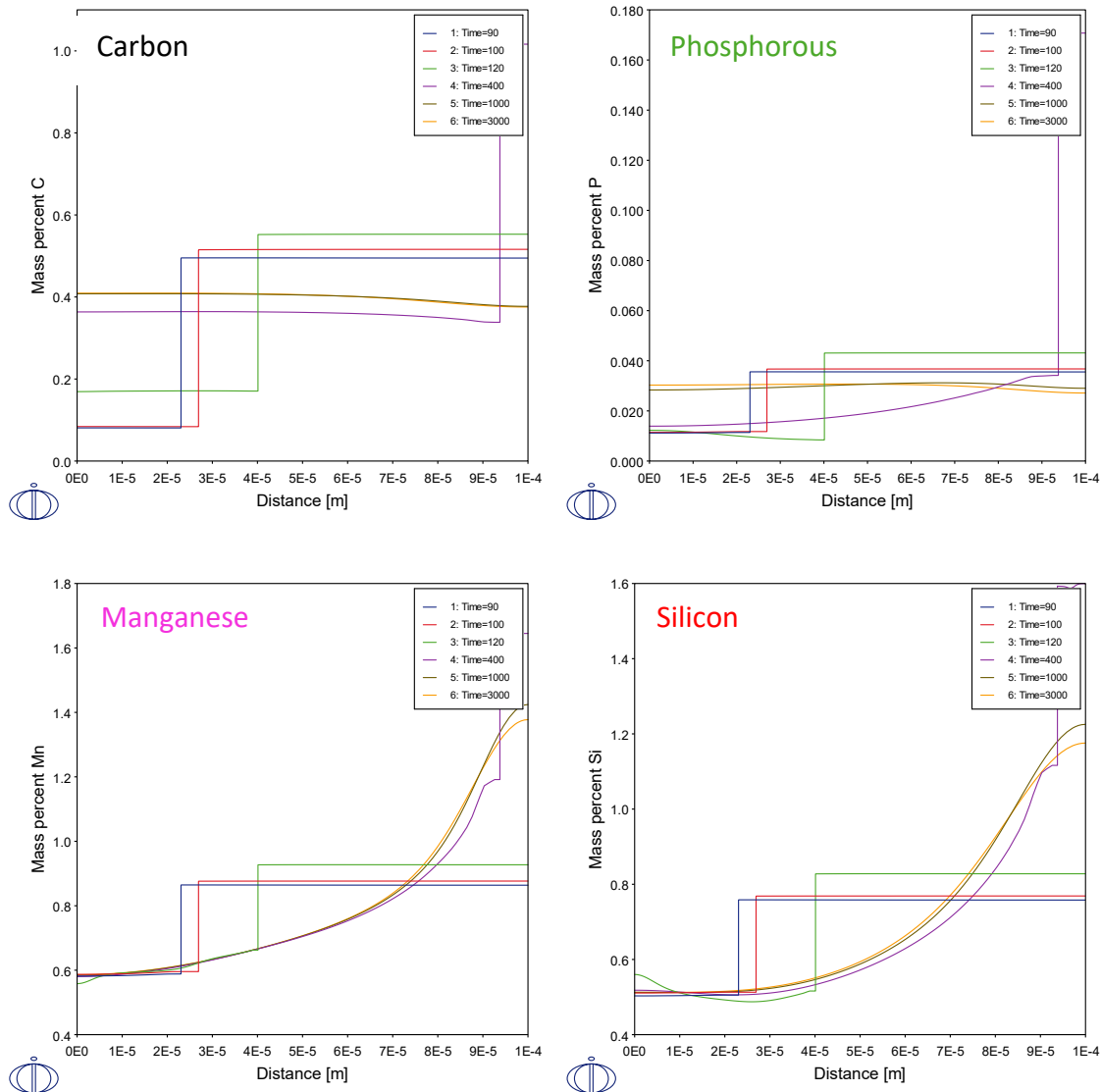

Figure 7. Evolution of concentration profiles of all elements during solidification. The diffusion of carbon and phosphorous is so fast that segregation is quickly evened out after final solidification.

In metallurgy, segregation is often characterized using the segregation index S. I. This is simply defined as

$$S.I. = \frac{C_i}{C_0}$$

Where C_i is the locally measured concentration of some element and C_0 is the bulk concentration of the same element. This formula is mostly used for carbon segregation, but it can be used for any element.

The segregation of all elements across two secondary dendrite arms is shown in Figure 8. The mechanism of the experimentally observed peak shift of Phosphorous can now be well explained: Immediately after final solidification, Mn, Si, and P are positively segregated in the final melt pool in the interdendritic region. The diffusion of Mn and Si is so slow that the concentration peaks are only slightly decreased. The diffusion of P, on the other hand, is fast enough that after 3000 seconds the activity (which is the driving force for diffusion, and **not** the concentration) is completely homogenized (Figure 9). The elements Mn and Si increase the activity of P. This means that P diffuses away from regions with high Mn and Si concentrations. Redistribution of P is therefore completely controlled by the diffusion of Mn and Si. This, finally, is the explanation for the experimentally observed peak shift of P that might seem counterintuitive at first.

It should further be noted that C behaves similarly to P, except that the diffusion is so fast that the positive segregation is evened out only seconds after final solidification.
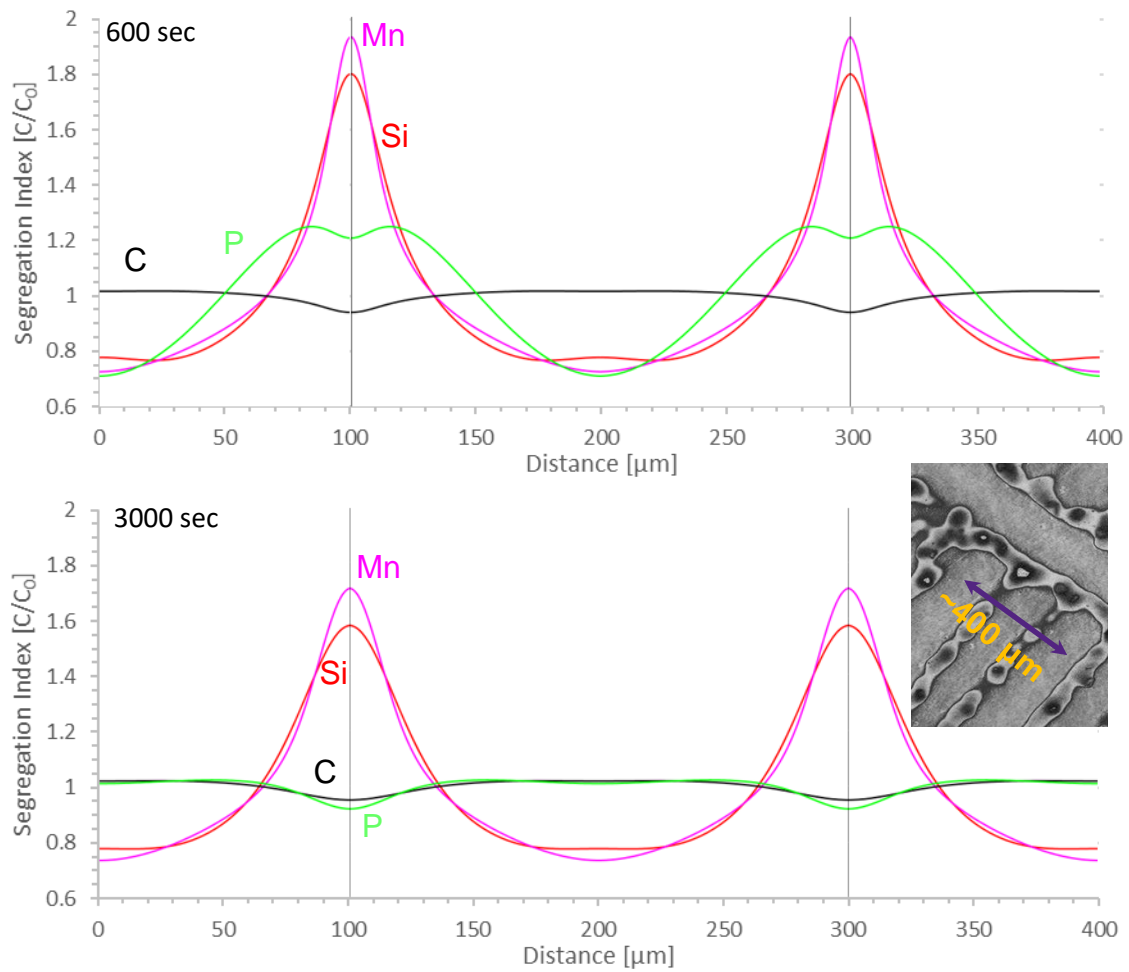
Figure 8. Calculated segregation of all elements just after final solidification (600 sec, top) and after cooling to 900 °C (3000 sec, bottom): just after final solidification there is positive P segregation in the final solidification pools between the dendrite arms. On further cooling, P redistribution is controlled by slow Mn and Si diffusion resulting in the unexpected, but experimentally observed, peak shift and negative P segregation.
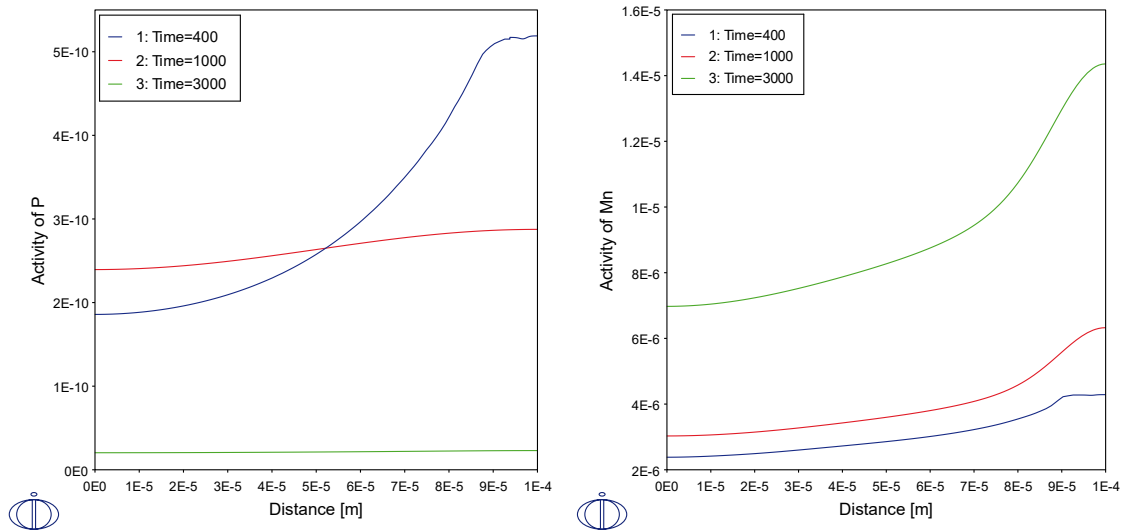
Figure 9. The diffusion of P is fast enough to completely homogenize the P-activity after 3000 sec (left). The diffusion of both Si and Mn is so slow that activity and concentration gradients are preserved (right). Both Mn and Si increase the P-activity. Therefore, with constant P activity, the P concentration will be lower in regions with high Mn and Si concentrations and P redistribution is controlled by Mn and Si concentrations at later stages. This is the explanation of the experimentally observed peak shift.