The Dark Arts of Perple_X and C-O-H Fluids

The thermodynamic data files used for these exercises are at:
www.perplex.ethz.ch/lausanne/lausanne.zip

Day 1: Run BUILD to define a *p*-*T* phase diagram Schreinemakers projection calculation for the siliceous dolomite system CaO-MgO-SiO_2-H_2O-CO_2. Answer no (or simply press enter) in response to any prompts that you not understand after reading the following sentence. Use the thermodynamic file hp02ver.dat; do not specify saturated fluid or components; select fluid equation of state #5 (CORK); use Convex-Hull minimization (computational mode 1); T = 733-983 K; p = 500-14500 bar; for simplicity exclude spu, ty, mont, merw, lrn and ak (high *T* calc-magnesio-silicates); answer yes to the “include solution model” prompt; specify the solution model file solution_model.dat and choose the solution model F (an H_2O-CO_2 fluid).

Verify the following options are set in perplex_option.dat: variance 1 1; initial_resolution 0.05; auto_refine_factor_II 2; pc_perturbation 0; short_print off; reaction_format stoich. Explanatory Note: The variance setting prevents the computation of high variance phase equilibria; the initial_resolution, auto_refine_factor_II and pc_perturbation settings assure that fluid pseudocompounds will be generated at exact (pc_perturbation = 0) compositional intervals of δ = initial_resolution/auto_refine_factor_II = 0.025 mol % CO_2 and therefore that singular equilibria at fluid compositions that are an integral multiples of δ will be computed by VERTEX. VERTEX will output reaction stoichiometries and lists of equilibrium coordinates if reaction_format = stoich and short_print = off and a print file has been requested in the problem definition file (e.g., my_project.dat). These settings are convenient for the present calculation and, with the exception of pc_perturbation = 0, will not cause no problems for other types of calculations. In calculations with more than one solution model setting pc_perturbation = 0 is ill-advised.

Calculate the phase diagram projection with VERTEX. Run PSVDRAW to generate a PostScript plot of the projection, close your eyes and view the plot in your preferred graphical viewer/editor (e.g., Ghostview, CorelDraw, Adobe Illustrator), verify that the plot is incomprehensible, if the plot is comprehensible then try squinting. Then use PSVDRAW to display only fluid-absent equilibria, by answering yes to the “Restrict phase fields by phase identities”, these equilibria (and their metastable extensions, which would be computed if you did the calculation excluding H2O and CO2 as endmembers) define the absolute stability of various reactant and product assemblages, e.g., di + mag + atg cannot be stable, regardless of whether a fluid is present or not, at pressures below that of the di + mag + atg = fo + tr + dol equilibrium (in fact, the assemblage is only stable under fluid-absent conditions).

(a) By answering yes to the “Restrict phase fields by phase identities”, use PSVDRAW to display the stability fields of di + atg + dol and tr + fo + cc (you can only do one at a time), where are these assemblages stable with fluid? To make the plot more legible answer yes to the PSVDRAW prompt “Modify default equilibrium labeling”, then instruct PSVDRAW to use text labels for curves longer than 25% of the axis length and to use numeric labels for curve longer than 4% of the axis length. The lists of equilibria at the end of print file (e.g., my_project.prn) provide the key for the numeric univariant curve and pseudo-invariant point labels.

(b) If you are not pressed for time, sketch the isobaric T-X_{CO2} Schreinemakers invariant point projections that correspond to the di + do + tr + cc + fo + F univariant field that limits the high temperature stability of cc + fo + tr in part (a) at pressures of 3 kb and 0.5 kb. The volatile stoichiometries of the five isobaric T-X_{CO2} univariant fields are:

(di) do + tr = fo + cc + 8 H_2O + 9 CO_2
(do) cc + tr = fo + di + 3 H_2O + 5 CO_2
(tr) di + do = cc + fo + CO_2
(cc) do + tr = di + fo + 2 H_2O + 5 CO_2
(fo) tr + cc = do + di + H_2O + CO_2

use the volatile stoichiometries and the invariant fluid composition, from part (a) to locate the singular points (extrema) on the stable or metastable section of each curve. Sketch the chemographic phase relations (i.e., a CaO-MgO-SiO_2 composition phase diagram) that corresponds to each sector about the T-X_{CO2} invariant points.

In a siliceous dolomite contact aureole about a granite (a source of water-rich fluid) you observe the following sequence of mineral assemblages

vein -> fo + di + cc -> fo + di + do -> di + do + tr -> marble

about veins on a sufficiently small scale that is reasonable to assume the zones developed at constant pressure and temperature. Given your knowledge of how the T-X_{CO2} invariant point topology corresponding to the di + do + tr + cc + fo + F univariant field changes as a function of pressure locate the field within the p-T projection in which the mineral assemblages could have developed. What is the possible range of X_{CO2} for the vein fluid?

(c) If you skipped (b), or you just want to check your p-T-X_{CO2} Perple_X skills: Calculate isobaric T-X_{CO2} Schreinemakers projections for the CaO-MgO-SiO_2 system at 3 kb, and 0.5 kb. If you run BUILD to create the problem definition file for these calculations, then the input is identical to that for the previous p-T projection except: respond yes to the saturated fluid, specify both H2O and CO2 as components of the fluid; choose fluid equation of state #5; choose T and X_{CO2} as independent variables and, for simplicity, restrict the temperature range to 723-923 K; and respond no to the “include solution model” prompt. Locate the tr + fo + cc stability field, i.e., the tr + fo + cc + F field part (a), in each T-X_{CO2}, verify the relation between invariant and singular points of the T-X_{CO2} diagram to the univariant and singular curves of the p-T diagram (note that the p-T diagram shows only singular curves for which the fluid composition is an integral multiple of δ_{CO2}, if you are a glutton for punishment you can compute the missing singular curves with FRENDLY and superimpose them on the p-T diagram). Calculate composition diagrams in each sector immediately about the tr + fo + cc + di + do T-X_{CO2} invariant point at 3 and 0.5 kb. The input to BUILD for this calculation is identical to that for the T-X_{CO2} diagram calculation except that you specify 0 independent potentials after choosing Convex-Hull minimization. The results can be plotted with PSVDRAW. Given your now extensive knowledge of the tr + fo + cc + di + do + F phase relations solve the problem posed in the latter part of (b). The beauty of this analysis is that it does not require or assume the system has a fixed non-volatile composition. However, if you feel overwhelmed by the task or simply wish to experiment further with isochemical phase diagram sections you can solve the problem by computing isobaric-isochemical T-X_{CO2} diagram sections (aka pseudosections) for a bulk composition of 0.333 mol SiO2, 0.317 mol CaO, and 0.350 mol MgO. The input to BUILD for this calculation is identical to that for the T-X_{CO2} projection except that you must specify computational mode 2 “Constrained minimization”. The result is plotted with PSSECT and you can recover information from the section with WERAMI.

(d) Construct isobaric-isothermal μ_{H2O}-μ_{CO2} Schreinemakers projections to view the fluid saturation surface for the CaO-MgO-SiO_2 system. To set this calculation up in BUILD you must: answer no to the saturated fluid phase prompt and yes to the “Use chemical potentials … as independent variable prompt”; specify Convex-Hull minimization with μ_{H2O} and μ_{CO2} as independent variables, set μ_{H2O} to vary from a maximum -290000 J/mol (slightly above the saturation value computed with FRENDLY) to a minimum -230000 J/mol (the maximum value less ~RTln[10^{-4}], the effect of reducing water activity to 10^{-4}) and set μ_{CO2} to vary from -459000 to -399000 J/mol; specify p-T sectioning conditions of 3 kb and 833 K; use solution models and select solution model “F” (fluid). IThe diagram is calculated with VERTEX and plotted by PSVDRAW. Verify that intersection of the various univariant equilibria with the fluid saturation surface correspond to the location of the univariant curves at 833 K in the T-X_{CO2} diagram calculated at 3 kb in part (c). If you wish to see how the H_2O-CO_2 solvus looks in an μ_{H2O}-μ_{CO2} lower the temperature of your calculation to ~523 K and change the fluid EoS from CORK (5) to the MRK (0).

Day 2:

(e) Use FLUIDS to compute the speciation of a graphite saturated C-O-H (EoS 10) and/or C-O-H-S (EoS 12) fluid at an arbitrary p-T-X_O condition (for simplicity, in the case of a C-O-H-S fluid choose the pyrite-pyrrhotite buffer). Then tabulate C-O-H fluid properties as a function of X_O at 1000 bar and 873 K, for legibility answer yes to the “output logarithmic values…” prompt. Plot the speciation (logarithmic proportions) using PSTABLE or the perple_x_plot MatLab script; separately, plot log(fO_2) and then the fugacities of H_2O, CO_2 , and CH_4. Note that at $X_O > 1/3$ the fluid is essentially a binary H_2O-CO_2 mixture and fO_2 differs little from the CCO buffer (i.e., the fO_2 at $X_O = 1$). If you like puzzles, then work out the relationship between X_O and X_{CO2} in the limit that the COH fluid is truly binary at $X_O > 1/3$. Repeat your tabulation at 500 K and again plot the fugacities of H_2O, CO_2, and CH_4, why are the fugacities no longer monotonic functions of X_O?

(f) In Perple_X graphite saturated C-O-H fluid equilibria may be treated two ways (see Chapter 6 of the "Perple_X Tutorial"). In one C is kept as vestigial component and while some calculations may be more intuititive, certain calculations (e.g., the transition from fluid-saturated to fluid saturated conditions) are not possible and the method is not rational. The rational alternative we will pursue here is to specify C as a saturated component, i.e., in petrologic parlance to project through C, in which case graphite saturated fluids become binary H-O mixtures and are exactly analogous to H_2O-CO_2 fluids, but with the advantage that we can retain information about redox state. The first step in this process is to run CTRANSF to transform the thermodynamic data base (hp02ver.dat) in terms of the conventional components CO_2, H_2O and O_2 into a data base in terms of H_2, O_2, and C necessary for the projection and while your at it transform FeO into Fe. Transform O_2 into C, i.e., $C = CO_2 – O_2$; then transform CO_2 into $O_2 = CO_2 – C$, H_2O into $H_2 = H_2O – ½ O_2$; and FeO into $Fe = FeO– ½ O_2$; when you transform CO_2 and H_2O CTRANSF will ask you if you want H_2 and O_2 to be "special components" (i.e., possible components of a saturated fluid), in each case answer yes. CTRANSF will name the transformed thermodynamic data base file "ctransf.dat", if you don't like the name, rename it.

(g) Repeat the metacarbonate petrogenetic grid calculation of the previous days, using the transformed data base file, specifying C as a saturated component and H_2, O_2, CaO, MgO and SiO_2 as thermodynamic components; exclude spu, ty, mont, merw, lrn, ak, CH_4, CO, CO_2, and H_2O; answer yes to the "include solution model" prompt; specify the solution model file solution_model.dat and choose the solution model GCOHF (an H_2-O_2 graphite saturated fluid). Compare the results, the differences are minor and reflect that graphite leads to only a minor reduction in H_2O and CO_2 concentrations under oxidized ($X_O > 1/3$) conditions. The graphite saturated calculation effectively has coarser resolution because an increment of δ in X_O, corresponds to roughly 3/2 of the same increment for X_{CO2}. Next repeat the calculation outlined in (c), but now as T-X_O diagram for graphite + fluid-saturated conditions using fluid equation of state #10, answer yes to the "compute $f(H_2)$ and $f(O_2)$ as the dependent fugacities" prompt. Verify the location of the singular points of the equilibria mentioned in (c). Given that the model system has only stoichiometric minerals, fluid can be generated from a fluid absent condition only at the conditions of invariant and singular T-X_O points. This requirement in combination with the stability of carbonates in reduced fluids ($X_O < 1/3$) has the interesting implication that devolatilization of a carbonate rock can generate extraordinarily reduced fluids, e.g., the cc + br + per + dol T-X_O invariant point corresponds (as can be verified from the petrogenetic grid) to the reaction cc + br + gph = per + dol + F. This potential, of course, requires the right bulk compositions.

(h) A disadvantage of fluid-saturated calculations is the assumption that all compositions of the fluid are stable, this is certainly not true in C-O-H fluids at low temperature because of immiscibility. One way around this problem is to make a phase diagram section which the amounts of the fluid components are so large that the bulk volatile composition of the system will not be effected significantly by solids. To illustrate this for the graphite-saturated ultramafic system construct an isobaric phase diagram section as a function of fluid.

Run BUILD. Use the thermodynamic file from (f) (ctransf.dat); do not specify a saturated fluid, specify carbon as a saturated component, and specify MgO, Al_2O3, SiO_2, CaO, Fe, O_2 and H_2 as thermodynamic components (drop CaO and Al_2O_3 if you want the calculation to go fast); select fluid equation of state #10, answer yes to the "compute $f(H_2)$ and $f(O_2)$ as the dependent fugacities" prompt; use constrained minimization (computational mode 2); select X(C1) as the *x*-axis variable, *T* (573-973 K) as the *y*-axis variable, and a pressure of 2 kb; when prompted for composition C0 enter 0.9896 0.0142 0.6707 0.0214 0.0913 0 10 (reduced lherzolite, remember to delete the CaO and Al_2O_3 values if you omit these components), and for composition C1 enter 0.9896 0.0142 0.6707 0.0214 0.0913 10 0 (oxidized lherzolite); exclude CH4, CO, CO2, H2O, spu, ty, merw, lrn, spr4, and ak (these phases might actually be important at extremely reduced conditions); include solution models GCOHF, Atg(PN), Chum, Do(HP), M(HP), B, Wus, Anth, Tr, Opx(HP), O(HP), Chl(HP), Omph(HP), T, and Sp(HP).

If you want the results to look nice set the following options in perplex_option.dat: auto_refine_factor_I 4; global_reach_increment 6; initial_resolution 0.04; solvus_tolerance_II 0.05.

Run VERTEX and plot the result with PSSECT. As in (g) carbonates (and magnetite) are stable at reduced fluid compositions, which demonstrates that prograde metamorphism of normal serpentinites is capable of generating reduced fluids. These fluids are reduced by the formation of the oxygen rich carbonates (and magnetite). However, the carbonates and ferric iron minerals do not seem to coexist with iron, thus a more complicated process (or better data) is required to explain the presence of alloys in ultramafic rocks.

(i) Carbon solubility increases with temperature and decreases with pressure, thus it is possible that continuous variation of physical conditions during the upward migration of C-O-H fluids with the Earth can induce carbon precipitation or dissolution. However, such effects are likely to be weak (Connolly & Cesare 1993). In contrast, chemical effects caused by introducing a metasomatic fluid that is not in equilibrium with the host rock are potentially profound. If the problem is to find a mechanism of precipitating carbon from an oxidized H_2O-CO_2 fluid or to generate a reduced fluid, the somewhat counterintuitive solution is to find conditions at which oxidized (carbonates) minerals will precipitate from the metasomatic fluid. This is best understood by mapping stable mineralogies on the C-O-H fluid composition space (Connolly 1995); however, in my initial attempts to do this I used a cumbersome formulation (EoS #20). Recently, I added a true ternary C-O-H fluid model to Perple_X that, in principle, simplifies such calculations because it assumes neither C nor fluid saturation and can therefore be used like any other solution model (you can experiment with the model separately in FLUIDS by choosing EoS #27). I say in principle, because although setting up the calculation is simple, the results which span essentially all possible redox states can be exceedingly complex.

For this final exercise we follow the strategy of part (h) in that we make a composition diagram for volatile dominated bulk compositions so that the bulk composition of the system is effectively the fluid composition, yet the diagram will show the mineral assemblages for the lithology of interest (dunite in this example).

Run BUILD. Use the thermodynamic file from (hp11ver_metal.dat); do not specify any constrained components, specify MgO, Si, Fe, C, H_2, and O_2 as thermodynamic components; if you are prompted for a fluid equation of state select #0; use constrained minimization (computational mode 2); select X(C1) as the *x*-axis variable, select X(C2) as the *y*-axis variable, a temperature of 773 K and a pressure of 30 kb (a plausible condition at the slab-mantle interface during subduction?); enter 0.9896 0.6707 0.0913 1e-3 10 1e-3 for composition C0, enter 0.9896 0.6707 0.0913 1e-3 1e-3 10 for composition C1, and 0.9896 0.6707 0.0913 10 1e-3 1e-3 for composition C2; exclude CH_4, CO_2, CO, H_2O, Fe_7C_3, afchl, phA, and cen; include solution models COHF, Atg(PN), Chum, M(HP), B, Wus, Anth, Opx(HP), O(HP), T, Sp(HP), MF, FeSiC-BCC, and FeSiC-FCC.

Because this calculation may take a long time, set auto_refine man in perplex_option.dat. This setting will halt the calculation after the exploratory stage and allow you to inspect initial results to verify that you have set the problem up correctly (or at least not wildly incorrectly). If everything looks reasonable start the final calculation. If you want the results to look nice (but the calculation may take more than 30 minutes) set the following options in perplex_option.dat: auto_refine_factor_I 4; global_reach_increment 6; initial_resolution 0.04; solvus_tolerance_II 0.05. Plot the result with PSSECT, locate the carbon saturation surface and compositions of the volatile species, in a separate plot locate the conditions at which alloy (FeSiC(BCC)) and metallic compounds (mos [SiC], FeSi, Si-diam [Si]) become stable. While it is reasonable to expect that fluids released by devolatilization of oxides, carbonates and hydroxides/hydrates will generally have H/O ratios less than two (cf part (g)), organic volatile sources (e.g., kerogen) have H/O ratios substantially greater than two.

A few years ago it was proposed in a Nature paper that the H_2-H_2O solvus (visible at low X_O in the present results) provides a mechanism for generating ultra-reduced fluids, what is the flaw in that proposition?