D-COMPRESS

Volatile species partition in magmas

USER MANUAL

Version 2015

1. Introduction

This user manual describes the software D-Compress, which calculates volatile species partition in magmas. It computes the gas and melt volatile composition of five volatile systems (O-H, S-O-H, C-S-O-H, C-S-O-H-Fe, and C-O-H). The chemical system considered is composed of at most nine volatile species (H_2O, H_2, O_2, SO_2, H_2S, S_2, CO_2, CO, and CH_4). The current version has been calibrated so as to simulate the volatiles coexisting with three common types of silicate melts (basalt, phonolite, and rhyolite). Operational temperatures depend on melt composition and range from 790 to 1400°C, and pressure ranges from atmospheric to 3000 bar.

Theory, use, and limitations of D-Compress are described in Burgisser, A., Alletti, M., and Scaillet, B. (2014) *Simulating the behavior of volatiles belonging to the C-O-H-S system in silicate melts under magmatic conditions with the software D-Compress*, Computers & Geosciences. Table 1 at the end of this user manual summarizes the variable symbols used in this paper and how they are referred to in the output files. Table 2 lists the compositions of the melts used to calibrate the solubility relationships (species fugacity – species melt content).

Two types of solutions can be searched for with D-Compress. The first is finding the equilibrium conditions of all species when only a subset of variables is known. The second type of resolution is to change pressure by compression or decompression while assuming mass conservation of the atomic elements. The two following section explain how to use these capabilities, and the last section deals with convergence issues.

2. Fixed pressure calculations and input parameters

D-Compress enables the user to calculate the gas and melt volatile composition of 5 systems: O-H, S-O-H, C-S-O-H, C-S-O-H-Fe, and C-O-H. These are selected in the panel labeled "Chemical system" in the upper left of the main window (Fig. 1).
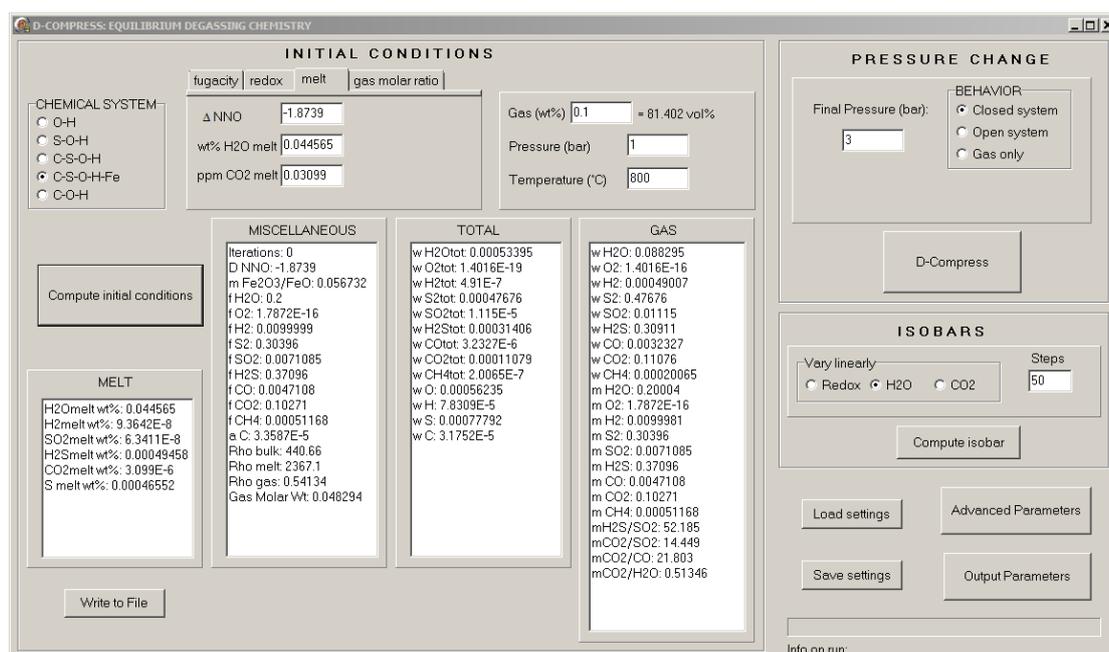
Figure 1: Main window of D-Compress.

For all systems, at least 3 input parameters are needed to establish the gas and melt volatile composition: gas weight fraction, pressure, and temperature. These are grouped in the central box (Fig. 1). Depending of which system is selected, there are up to three additional parameters that need to be set. There are three ways to input these parameters (Fig 2). The user can choose between entering the fugacities of H_2, H_2O, and CO_2 (tab "fugacities"), entering the redox state and the fugacities of H_2O and CO_2 (tab "redox"), entering the redox state and the melt content of H_2O, and CO_2 (tab "melt"), and entering a combination of ratios of gas species fugacities (or molar proportions) of CO_2, CO, SO_2, H_2O, H_2S, and OCS (tab "gas molar ratio").

Figure 2: *The four different ways to select species-related inputs in D-Compress.*

In the main window (Fig. 1), the button "Compute initial conditions" calculates all the other relevant parameters of the system selected. Note that hitting the Enter key when editing any field of the input Parameters panel ("f H2O", "Pressure", etc.) is equivalent to clicking on "Compute initial conditions". Results are displayed in 4 separate lists labeled "MELT", "TOTAL", "MISCELLANEOUS", and "GAS", respectively. The amount of information on each list is controlled through the "Output parameters" button on the lower right of the main window (Fig. 3). The button "Write to file" records the four lists into a text file, and the buttons "Load settings" and "Save settings" store all the input parameters.
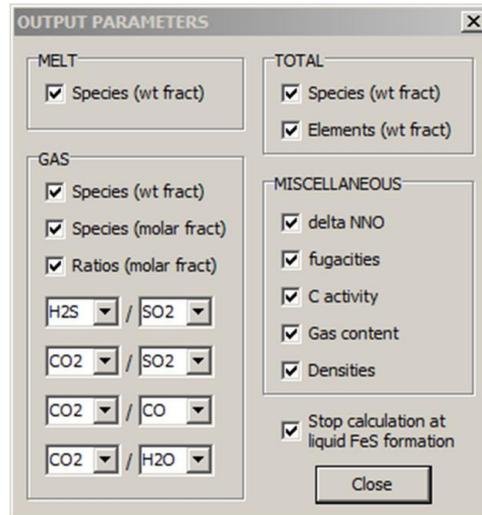
Figure 3: D-Compress window allowing the user to modify the output parameters.

When trying to match a target value that is not a preexisting input parameter, such as the S melt content or a molar ratio of gas species not listed, it is important to remember that all volatile systems have an asymptotic behavior of the fugacity values when their sum is approaching the total pressure. This can be illustrated with the default phonolitic melt at 1080 °C, 2000 bar, $f\,H_2$ = 0.1 bar, and $f\,H_2O$ = 1000 bar in the C-S-O-H-Fe system. If $f\,CO_2$ is set to 1600 bars, the molar ratio CO_2/SO_2 is 31.083 in the gas phase. Increasing $f\,CO_2$ to 1651.4 bars causes CO_2/SO_2 to reach 5159.6. Further increase of $f\,CO_2$ by 0.1 bar (i.e. 1651.5), however, causes the sum of gas molar fractions to exceed one. As a result, the four output lists are masked to the user and a warning message indicates that some fugacities are negative so that they to add up to the total pressure. The steep increase of CO_2/SO_2 for a small change of $f\,CO_2$ is typical; an arbitrary high value of CO_2/SO_2 can be obtained by increasing $f\,CO_2$ close to but below 1651.5 bars.
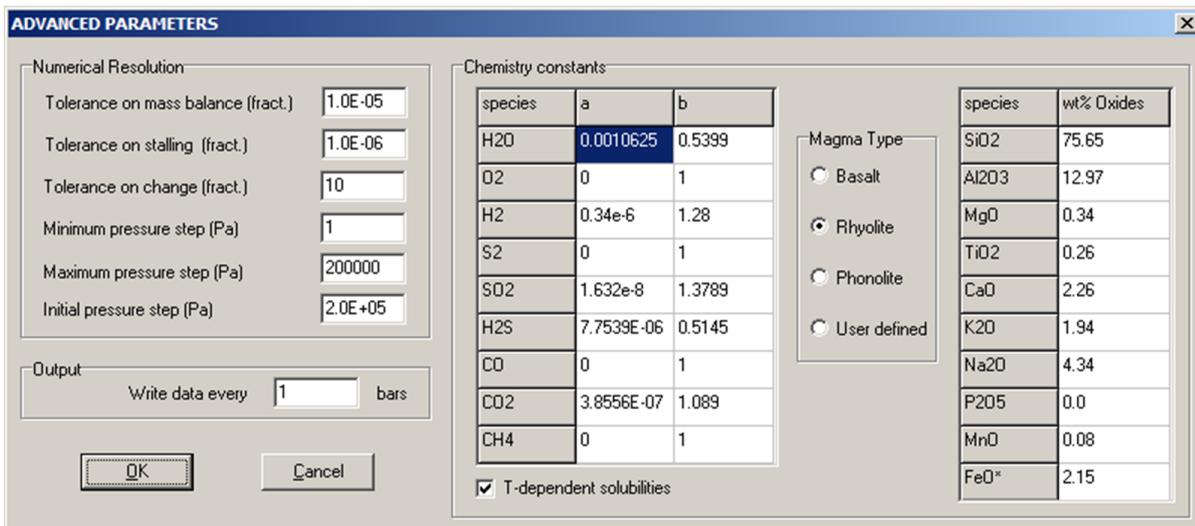
Figure 4: D-Compress window allowing the user to modify advanced parameters.

The type of melt is selected through the "Advanced parameter" button on the lower right of the main window (Fig. 4). The box labeled "Magma type" allows the user to select one of three pre-defined melt compositions: basaltic, rhyolitic, or phonolitic. This affects the solubility laws. When rhyolitic melt is selected, the user has the choice between fixed and temperature dependent solubilities. In the latter case, the software enforces the temperature range over

which these relationships are valid (790 - 910 °C). Phonolitic melts have fixed solubility coefficients that were determined at ~1000 °C (Table 2), except for H_2O when temperature-dependent solubilities valid from 825 to 1200 °C can be selected. When a basaltic melt is selected, the user has the choice between fixed solubility coefficients and coefficients for H_2O and CO_2 that vary according to temperature (1000 - 1400 °C) and composition (see below). For all melts, changing the proportions of the major oxides affects the relationship between m_{Fe2O3}/m_{FeO} and fO_2. Such changes are thus only apparent in compression/decompression runs. Entering a user-defined melt composition and/or solubility law is also possible. User-defined parameters can be saved and retrieved using the "Load settings" and "Save settings" buttons of the main window.

When a basaltic melt is selected, the user has the choice between fixed solubility coefficients and coefficients for H_2O and CO_2 that vary according to temperature and composition. In the latter case, the model of Iacono-Marziano et al. (2012) is used to calculate the values of a_{H2O}, b_{H2O}, a_{CO2}, and b_{CO2} by recasting their semi-empirical formulation so that it follows the Henrian behavior (Eq. 7 in Burgisser et al., 2014). This recasting takes the form $w_{Ti\,melt} = a_i \gamma^{b_i} (m_i P)^{b_i}$ to take advantage of the fact that the formulation of Iacono-Marziano et al. (2012) depends on the partial pressures of H_2O and CO_2 ($m_{H2O}P$ and $m_{CO2}P$, respectively). As a result, both a_{H2O} and a_{CO2} depend on pressure, temperature and melt composition. The coefficient a_{CO2}, however, also depends on a_{H2O} because Iacono-Marziano et al. (2012) used a semi-empirical regression for CO_2 solubility that is a function of the dissolved molar fraction of H_2O. This inter-species solubility dependence introduces a slight inconsistency with the Henrian behavior assumed in equation (7). This inconsistency has a minor effect on model outputs (typically <1% on the CO_2 melt content at a given melt H_2O content), and isobars in the melt H_2O vs. melt CO_2 space are nearly identical for both models under most redox conditions ($\Delta NNO \geq -2$). Under more reduced conditions, however, D-Compress calculates CO_2 melt content inferiors to those predicted by Iacono-Marziano et al. (2012) because D-Compress takes the presence of reduced, insoluble species (CO and CH_4) into account (Scaillet and Pichavant, 2004). In all cases, D-Compress enforces the temperature range over which these solubility relationships are valid (1000 - 1400 °C).

Isobar calculations are possible when initial conditions are set so that melt volatile content are used as input (tab "melt", Fig. 2). To start such a calculation, the user must select which of redox, H_2O, and CO_2 will be varied over how many steps (panel "Isobars" on the right of the main window, Fig. 1), as well as between which bounds the linear variation will take place. The number of steps does not affect the precision of the output. All output values are set to zero if a given step yields unphysical input parameters (e.g., a water content of 10 wt% for an isobar value of 1000). Isobar output parameters are predefined and cannot be changed; the file contains the melt amounts of the soluble species, the pressure, the temperature, the redox state, and the gas composition in molar fraction.

3. Compression/Decompression calculations

The parameters controlling the compression or decompression calculation are selected in the panel labeled "Pressure change" in the upper right of the main window (Fig. 1). They consist of the final pressure and which type of run will be performed: "Closed system", "Gas only", or "Open system".

Closed system runs assume that the gas is in equilibrium with the surrounding melt. There is no physical segregation between gas and melt, like in the case of a rising viscous bubbly melt, or a gas slug surrounded by a thin melt shell.

Gas only runs ignore volatile contribution from the melt. They are carried out by setting all solubility coefficients to zero and fixing the gas content to 100 wt%. The output file, however, includes melt volatile contents that are recalculated a posteriori using the fugacities given by the pure gas compression/decompression. These melt volatile content can either be disregarded or considered to represent a stagnant melt through which the gas is passing. One option is to reach the target pressure in an isentropic fashion, which causes the temperature to change at each pressure step (Fig. 5). The main window indicates the temperature that will be reached at the final pressure. The user can change the heat capacity ratio. The default value is 1.2, which corresponds to a mixture of H_2O and CO_2 in equal proportions at 1000 °C.
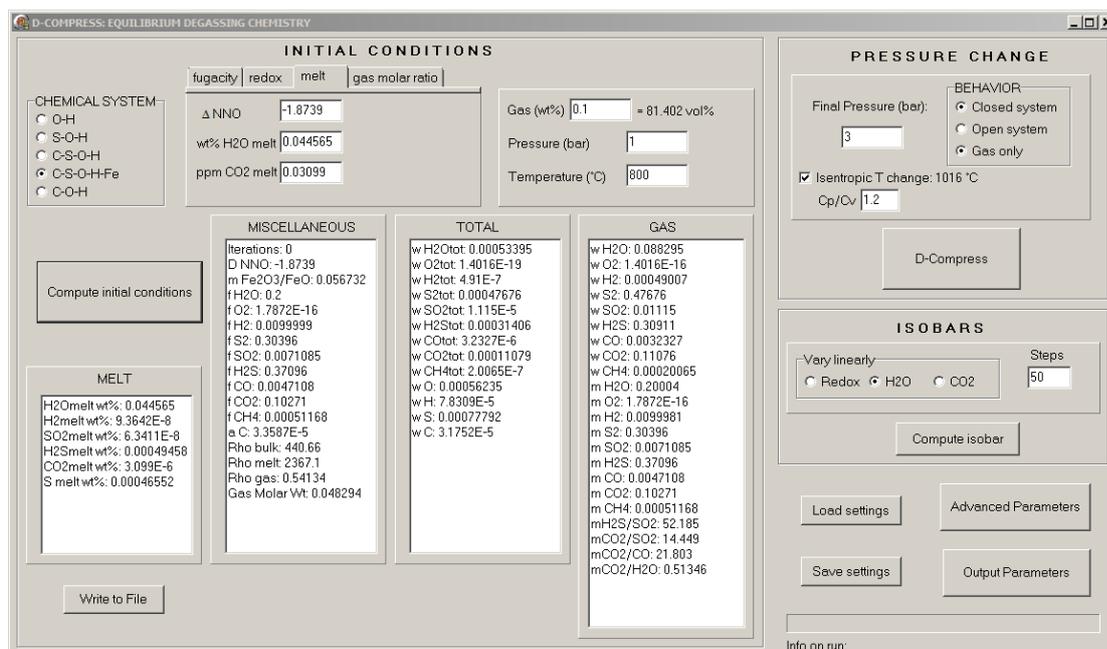
Figure 5: Main window of D-Compress with gas-only isentropic temperature changes.

Open system runs in decompression closely approach the conventional Rayleigh distillation. At each pressure step, an aliquot of gas is removed so that the small but finite value of gas fixed in the initial conditions (typically ~10^{-6} wt%) remains for the next step. How much gas was lost at each pressure increment is recorded in the output file. Compression runs in open system directly involve the gas aliquots discarded at each step, the composition of which is unknown a priori. The compression algorithm simply assumes that these aliquots have the same composition as the remaining gas at that pressure step when it increases the gas content back to the fixed, initial value set in the initial conditions. During decompression runs, if the porosity is above 10 vol% at any given pressure, the behavior of the run is leaving the open-system degassing realm to enter that of closed-system degassing. This can be prevented by decreasing the initial amount of gas and/or decreasing the maximum pressure step in the "Advanced parameters" window.

Often several styles of decompression will be run from the same starting conditions. Some combinations of input panel and decompression styles are incompatible (e.g., "Melt" with "Gas only", so switches between input panels might be necessary. Assume, for instance, that the input panel was set on "melt" for a "Closed system" decompression. Now, to run a "Gas only" decompression, the following steps need to be done. First, make sure that the species fugacities are displayed in the output panel "GAS". Next, select "Gas only" decompression, which will trigger an automatic change of input panel from "melt" to "redox". Copy the values of f H_2O and f CO_2 from the output panel "GAS" to the corresponding fields of the input panel "redox". Then click on "Compute initial conditions. The values of the parameters in the output panels

(fugacities, molar fractions, etc.) should not change, except some last digits because of round off issues. The "Gas only" decompression can now be run ("D-Compress button") with the same initial conditions as the "Closed system" run.

Parameters governing the numerical resolution of compression/decompression runs are selected in the left box of the "Advanced parameters" window (Fig. 4). Three parameters control the pressure steps. The algorithm takes the initial step (typically 1/1000 of the initial pressure) and varies it between a maximum (typically 1/100 of the maximum pressure reached during the run) and a minimum (typically 1 Pa) value. Every 5 successful iterations, the pressure step increases by 20%, whereas every failed iteration causes the step to decrease by 20%. Considering the small values often taken by the pressure step, it is convenient to select a reasonable pressure increment, such as 0.1 or 1 bar, for the output file to be recorded. Three parameters control numerical accuracy. The numerical resolution involves finding the roots of at most three equations. In the S-O-H-C-Fe system, these equations correspond to the mass balance of S, O, and H, which are resolved iteratively to the accuracy prescribed by the value of the "Tolerance on mass balance" (typically 10^{-3} – 10^{-7}). The variables solved for are the carbon species molar fractions (m_{CO2}, m_{CO}, m_{CH4}). From one iteration to the next, the changes in these molar fractions should be at least the value of the "Tolerance on stalling" (typically 10^{-3} – 10^{-7}) and at most the value of the "Tolerance on change" (typically 0.5 – 100). Three entries of the output file can be used to track run quality (Table 1): pressure step, number of iteration per step and reason for success, and errors on mass balance, which are given by subtracting the initial amounts of atomic species to those of the current step.

4. Convergence issues

There are several reasons for a run to fail reaching final pressure. At every pressure step, the activity of carbon is calculated, and the run stops with an error message if it reaches unity because carbon precipitation is not taken into account by the model. If a compression run terminates normally before the final pressure, it may have run out of gas. This may be checked for by looking at the final value of w_{gT} and avoided by increasing its initial value or that of the final pressure. Open-system, decompression runs terminating without apparent reason face a similar issue. When the gas fraction becomes very small, the aliquot removed becomes vanishingly small, sometimes exceeding machine precision. Here also, increasing the initial w_{gT} should allow the run to finish. Although mass conservation is ensured from one pressure step to the next, there are no globally conserved quantities in an open-system run. Errors on total amounts of elements, which are given in the output file, should thus be minimized so that no long-range drift occurs. It is advisable to carry open-system runs with different tolerance levels to check that a given set of numerical convergence parameters yields sufficient accuracy.

These problems are generally solved by copying/pasting the values of f_{H2}, f_{H2O}, f_{CO2}, P, and w_{gT} from the penultimate recorded step to restart the run while using a combination of smaller initial or maximum pressure step, higher tolerance on mass balance, and lower tolerances on change and/or stalling. Sometimes it may be necessary to record every calculated step to understand why convergence is failing. This is done in the "Advanced parameters" window by having the same values in the "Minimum pressure step", "Maximum pressure step", "Initial pressure step" fields, and that value divided by 10000 in the "Write data every" field.

5. Test files

One input data test file is provided (InputTest.ini). It can be loaded by using the "Load settings" button (Fig. 1). Clicking successively on "Compute initial conditions" and "Write to File" should give an output identical to that in the "OutputFixedP.txt" file. Clicking on the "D-Compress" button should give an output identical to that in the "OutputDecompression.txt" file.

6. References

Burgisser, A., Alletti, M., Scaillet, B., 2015. Simulating the behavior of volatiles belonging to the C-O-H-S system in silicate melts under magmatic conditions with the software D-Compress. Computers & Geosciences.

Dobson, P.F., Epstein, S., Stopler, E.M., 1989. Hydrogen isotope fractionation between coexisting vapor and silicate glasses and melts at low pressure. Geochimica et Cosmochimica Acta 53, 2723-2730.

Scaillet, B., Pichavant, M., 2004. Role of fO_2 on fluid saturation in oceanic basalt. Nature 430, doi:10.1038/nature02814.

Table 1: Meaning of variable names of the compression/decompression output files. There is no carbon error reported because C mass balance is solved to machine precision. Sulfur melt fraction is the addition of the corresponding values of dissolved SO_2 and H_2S.

Name in output file	Symbol	units	Description
P(bar)	P	bar	Pressure
DNNO	ΔNNO		Oxygen fugacity referenced to the Ni-NiO buffer
mFe2O3_FeO	F		Ratio of ferric to ferrous iron
fH2O, fO2, …	$f\,H_2O, f\,O_2, …$	bar	Species fugacities
CAct	-		Carbon activity
Porosity	α		Gas volume fraction
GasFract	w_{gT}		Gas weight fraction
GasFractOut	-		Gas weight fraction discarded in open system runs
RhoBulk	-	kg/m^3	Bulk density = $\alpha\rho_g + (1-\alpha)\rho_l$
RhoGas	ρ_g	kg/m^3	Gas density = MP/RT
GasMolarWt	M	kg/mol	Gas molar weight
H2Omelt, O2melt, …	$H_2O_{melt}, O_{2\,melt}, …$		Species melt weight fraction
Smelt	-		Sulfur melt weight fraction
wH2O, wO2, …	$x_{H2O}, x_{O2}, …$		Species weight fraction in gas
mH2O, mO2, …	$m_{H2O}, m_{O2}, …$		Species molar fraction in gas
wH2Otot, wO2tot, …	$w_{TH2O}, w_{TO2}, …$		Species total weight fraction
wO, wH, …	$w_{TO}, w_{TH}, …$		Elements total weight fraction
mH2S_SO2, mCO2_SO2, …	$m_{H2S}/m_{SO2}, m_{CO2}/m_{SO2}, …$		Molar ratios of gas species
DP	-	Pa	Pressure step
Iteration	-		Number of iteration; negative number=stop on stalling or maximum correction, negative number=stop on mass balance
OError, HError, …	-		Error on mass balance= w_{TO}(initial) – w_{TO}(current)

Table 2: Composition (wt.%) of the melts used in calibrating D-Compress. Experimental run conditions and additional references are given in Burgisser et al. (2014).

Melt type	Reference	Sample[a]	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
Rhyolite	Clemente et al. 2004	MP synthetic	75.92	0.00	13.10	2.00	0.00	0.32	2.58	4.14	1.94	0.00
		MP18XII	72.06	0.00	12.43	6.99	0.00	0.29	2.45	3.93	1.84	0.00
		MP19XII	72.06	0.00	12.43	6.99	0.00	0.29	2.45	3.93	1.84	0.00
		Pinatubo	78.29	0.15	12.85	1.06	0.00	0.20	1.31	3.29	2.85	0.00
All	Gaillard et al. 2003	-	74.51	0.10	13.25	1.60	0.00	0.08	0.75	4.15	5.64	0.00
Rhyolite	Blank et al. 1993 with Dobson et al. 1989	-	77.70	0.07	13.00	0.38	0.04	0.05	0.52	4.08	4.19	0.00
Rhyolite	Fogel & Rutherford 1990	-	76.45	0.08	12.56	1.02	0.08	0.06	0.25	4.21	4.78	0.00
Rhyolite	Holtz et al. 1992, Holtz et al. 1995	AOQ	76.14	0.00	13.53	0.00	0.00	0.00	0.00	4.65	5.68	0.00
Rhyolite	Mangan & Sisson 2000	-	75.64	0.08	12.38	0.94	0.07	0.03	0.54	4.17	4.72	0.01
Basalt	Lesne et al. 2011a	VES-9	48.02	0.96	14.52	7.51	0.14	6.82	12.77	1.80	5.55	0.65
		ETN-1	47.59	1.66	17.19	10.15	0.17	5.72	10.85	3.42	1.98	0.51
		PST-9	49.40	0.80	15.80	7.64	0.20	8.00	12.70	2.30	1.90	0.40
Basalt	Lesne et al. 2011b	VES-9	48.67	0.97	14.72	7.62	0.14	6.82	12.94	1.82	5.63	0.66
		ETN-1	47.95	1.67	17.32	10.24	0.17	5.76	10.93	3.45	1.99	0.51
		PST-9	49.82	0.81	15.94	7.71	0.20	8.07	12.81	2.32	1.92	0.40
Basalt	Lesne et al. in review	VES-9	48.26	0.96	14.59	7.56	0.14	6.76	12.83	1.81	5.58	0.65
		ETN-1	47.41	1.65	17.12	10.13	0.17	5.70	10.81	3.41	1.97	0.51
		PST-9	49.40	0.80	15.80	7.65	0.20	8.00	12.70	2.30	1.90	0.40
Basalt	Beermann et al. 2011, Botcharnikov et al. 2011	Anhydrous	48.26	1.77	16.37	10.46	0.17	5.96	10.81	3.45	1.96	0.59
Phonolite	Schmidt & Behrens 2008	MBP[b]	59.84	0.65	18.67	3.50	0.17	0.34	0.77	9.72	5.65	0.00
		BS04/1	54.86	0.32	20.25	5.48	0.10	0.55	3.22	2.03	12.25	0.00
		BS04/2	58.23	0.33	20.26	5.62	0.09	0.55	3.46	4.21	6.42	0.00
		BS04/3	57.02	0.33	19.70	5.44	0.09	0.54	3.54	6.18	6.12	0.00
		BS04/4	57.11	0.33	20.35	5.61	0.10	0.57	3.63	8.20	3.09	0.00
		BS04/5	54.69	0.33	20.46	5.69	0.10	0.58	2.72	4.53	9.77	0.00
		BS04/6	56.00	0.31	19.29	5.32	0.09	0.53	1.91	4.96	10.38	0.00
		BS04/7	55.63	0.31	19.14	5.39	0.09	0.53	1.12	5.33	10.95	0.00
		BS04/8	53.64	0.35	20.52	5.74	0.11	0.59	0.38	5.75	11.56	0.00
		LSP-II[b]	59.55	0.19	22.41	1.64	0.35	0.07	0.71	9.36	4.75	0.00
Phonolite	Carroll & Blank 1997	MBP	59.38	0.66	18.92	3.46	0.20	0.33	0.79	10.07	5.55	0.07
Phonolite	Larsen & Gardner 2004	HAE2-1-95	58.39	0.31	23.09	1.39	0.00	0.14	0.84	8.62	6.84	0.00
		LST3-1-40	57.26	0.24	23.10	1.63	0.00	0.10	0.66	11.21	5.72	0.00
Phonolite	Burgisser et al. 2012	ERE+	55.54	1.12	19.26	5.42	0.25	1.04	2.52	7.74	4.82	0.49
Phonolite	Moncrieff 1999	MBPhon	59.87	0.66	18.96	3.49	0.20	0.33	0.79	10.10	5.53	0.08
Phonolite	Iacono Marziano 2005 with Iacono Marziano et al. 2007	-	57.15	0.30	21.34	2.70	0.14	0.39	3.26	5.16	9.46	0.09

[a] A dash means no sample name was given to the starting material.

[b] Runs at 845 and 850 °C were not taken into account.