

## CHOSETTO: a tool to compute degassing in the H<sub>2</sub>O-CO<sub>2</sub>-H<sub>2</sub>S-SO<sub>2</sub>-melt system

### PRELIMINARY NOTES FOR RELEASE v1

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**CHOSETTO.exe** is a windows-based program to compute degassing of H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S in magmatic melts. It also computes the FeO/Fe<sub>2</sub>O<sub>3</sub> redox ratio, the amounts of sulfur dissolved as sulfide and sulfate and thus the S-redox ratio.

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### HOW TO RUN

Download the zip file and extract all files in the same directory, wherever you want.

Open the Command Prompt (cmd.exe) from your Windows taskbar. By using basic DOS commands (e.g. "CD .." and "CD <directory\_name>" ) gets into the directory. Given your input composition and conditions (see below), simply type CHOSETTO and then press enter to execute the program.

### INPUT FILE (chosetto.dat)

The input contains the following columns (separator given by spaces)

- 1) P (Pa) (please note again: it's in Pascal)
- 2) T (K)
- 3) oxygen fugacity as  $\Delta\text{NNO}$
- 4) Total H<sub>2</sub>O in the system (weight fraction)
- 5) Total CO<sub>2</sub> in the system (weight fraction)
- 6) Total S in the system (weight fraction)
- 7) SiO<sub>2</sub>
- 8) TiO<sub>2</sub>
- 9) Al<sub>2</sub>O<sub>3</sub>
- 10) Fe<sub>2</sub>O<sub>3</sub>
- 11) FeO
- 12) MnO
- 13) MgO
- 14) CaO
- 15) Na<sub>2</sub>O
- 16) K<sub>2</sub>O

For consistency, please write composition as weight fraction of each oxide, with their sum (from 7 to 16) equal to 1 (anyway don't worry: there is renormalization, also if you add oxide percentages not closing to 100%)

After composition, you can put a note on the same line

Feel free to put down all the compositions you wish: just respect the above format or the code stops while reading a line with invalid format or also strange symbols not accepted by the code inherited by your editor. So, please use a very basic one.

### **DRIVER FILE (chosetto.ctr)**

This file allows you selecting options to run your calculation.

1<sup>st</sup> line. Two variables:

VAR1: put 0 for closed system calculation (melt+gas decompression) and 1 for open system degassing

VAR2: this is the quantity (mass fraction) of gas removed at pressure step if  $KVAR1 = 1$  (open system). Put a number between 0 and 1 (please look at the HINTS AND TRICKS section below)

2<sup>nd</sup> line. One variable:

VAR3: put 1 for using the input  $\Delta NNO$  to fix oxidation state at each calculation step or put 2 to use the input (mass)  $FeO/Fe_2O_3$  ratio or put 3 if you want to fix the  $fH_2S/fSO_2$  ratio

3<sup>rd</sup> line. Three variables:

VAR4 and VAR5: here you put the sample lines you want to run from the cosh.dat file. Put the numbers that you want from X to X+n, where  $n \geq 0$ . All the lines in the ranges will be processed, sequentially. IMPORTANT NOTE: the output file makes ONE file, does not put separators between samples at each input line. So, in the output it is up to you to discern the different compositions treated in your calculation (for example based on pressure steps). → I suggest ONE LINE per run, with creation of its own output file (it makes life easier).

VAR6: if it 1 you make a run at multiple pressure steps starting from the P given at that line in the cosh.dat file; if you put 0, you run the code just for the pressure given in the input file.

4<sup>th</sup> line. One variable :

VAR7: this is the  $fH_2S:fSO_2$  ratio, used only if  $VAR3 = 3$

### **OUTPUT FILE (chosetto.out)**

Pressure runs are made of 10 MPa steps down to  $P=200$  MPa, then every 5 MPa down to  $P=10$  MPa, then every 1 MPa down to  $P=5$  MPa and finally 0.5 MPa down to  $P=0.1$  MPa.

The output contains the following columns (from left to right):

- 1) P (MPa)
- 2) T (K)
- 3) Dissolved  $H_2O$  (weight fraction of the melt phase)
- 4) Dissolved  $CO_2$  (weight fraction of the melt phase)
- 5) Bulk dissolved S (weight fraction of the melt phase)
- 6) Exsolved  $H_2O$  (weight fraction of the gas phase)
- 7) Exsolved  $CO_2$  (weight fraction of the gas phase)
- 8) Exsolved  $SO_2$  (weight fraction of the gas phase)

- 9) Exsolved  $H_2$  (weight fraction of the gas phase)
- 10) Gas phase mass fraction (weight fraction of gas over gas + melt)
- 11) Gas phase volume fraction (volume fraction of gas over gas + melt)
- 12) Dissolved sulfur as Sulfide ( $S^{2-}$ ) (weight fraction of the melt phase)
- 13) Dissolved sulfur as Sulfate ( $SO_4^{2-}$ ) (weight fraction of the melt phase)
- 14) Sulfide/sulfate ratio (because involving sulfur as sulfide at numerator and sulfur as sulfate at denominator, molar and mass ratio are same)
- 15)  $\Delta NNO$
- 16)  $\log fO_2$
- 17)  $FeO/Fe_2O_3$  (mass ratio)
- 18)  $fH_2O$  (fugacity in the gas phase, in bar, NOT in MPa)
- 19)  $fCO_2$  (fugacity in the gas phase, in bar, NOT in MPa)
- 20)  $fSO_2$  (fugacity in the gas phase, in bar, NOT in MPa)
- 21)  $fH_2S$  (fugacity in the gas phase, in bar, NOT in MPa)
- 22)  $fH_2S/fSO_2$  (fugacity in the gas phase, in bar, NOT in MPa)
- 23)  $mH_{2S(g)}/mSO_{2(g)}$  (mass ratio of  $H_2S$  over  $SO_2$  exsolved in the gas phase)

## HINTS, NOTES AND TRICKS

While running, numbers appear on the screen: the pressure you see in bars and not in MPa.

When you open the output file, you probably must first change “D” in “E”, in order to have number to be recognized for their scientific format. This occurs typically if you use EXCEL.

Sometimes the code gets stuck: it normally occurs for the initial (or highest) pressure step, but not necessarily, although your expectations BASED on the  $H_2O+CO_2$  pressure estimations (e.g. via Papale et al., 2006) are that the melt you are looking at should be saturated.

This comes from numerical troubles in dealing with undersaturation when sulfur is added to  $H_2O+CO_2$ . This problem may in fact not occur for  $H_2O+CO_2$  only with the Papale et al., 2006 model. This is not the place to fully explain the issue, but basically this is due to the fact that when a gas exsolves from any liquid (gas and liquid at equilibrium), it MUST contain all the volatiles. Briefly, equilibrium thermodynamics of saturation implies that  $H_2O + CO_2 + H_2S + SO_2$  MUST BE COMPUTED.

Therefore, in many cases the melt would be saturated for  $H_2O$  and  $CO_2$  but because it is actually not for the total of sulfur in input, computation fails. It means that the FEW sulfur molecules that MUST be present in the gas (this a strict thermodynamic requirement ! ) are too few to be safely computed by the numerical routines, which then fails simply because all the sulfur is virtually still in the liquid and so routines do not achieve convergence for the equilibrium condition.

So, if you are undersaturated let's say for one component, you are actually undersaturated at all ( = no gas).

It is a tricky numerical problem which emerges when you approach the saturation for the total amount of components (normally sulfur) in input. Many times, the code deals with it, sometimes not. So, you need a total volatile amount in line with the full saturation for the highest (initial) pressures of you run

Note that worst cases are oxidized ones, i.e. for sulfur present mostly as sulfate.

So, you may play with some parameters (change total volatiles or lower P or change  $fO_2$ ). You can also go for the SOLWCAD Papale et al. (2006) model alone (no sulfur) (available at the INGV Pisa website) for early P-step and consider all S dissolved in the melt. In this case, please remember that there is a dilution effect

at least, and use a FeO and Fe<sub>2</sub>O<sub>3</sub> values for your separated H<sub>2</sub>O-CO<sub>2</sub> computation in line with those from the model here described, which contains the Moretti (2005) approach to iron oxidation, slightly modified.

Note that in a multi-step degassing process under open conditions (VAR1 = 1) you lay easily attain undersaturation in case you spill out too much gas fraction. Therefore, pay attention to the value you attribute to VAR2.

Finally, as explained in several papers (Moretti and Papale, 2004; Moretti and Stefansson, 2020; Moretti, 2021; Papale et al., 2021), the total amount of oxygen is not fixed, basically oxygen being intended as a perfectly mobile component.

## **MORE FEATURES**

Computation around 100 MPa and 500 MPa is inhibited because the SUPERFLUID equation of state (Belonovshko et al., 1992) around these values conjugates different working forms and problems can arise in both continuity and derivability. Therefore, if you are interested at pressure intervals around 100MPa and 500 MPa, please interpolate data calculated above and below.

By performing calculation, you'll certainly soon appreciate the role of TOTAL volatiles in determining the main features of the degassing trend that best explain your data (e.g. Mis). For further info please refer to Papale (2005) and Barsanti et al. (2009).

[THIS TOPIC IS IN PROGRESS AND WILL BE SOON AVAILABLE] CHOSETTO does not perform any check for attainment of saturation with respect to another S-bearing phase (e.g. pyrrhotite or FeS liquids). Therefore, it does not compute Sulfur Content at Sulfide Saturation (SCSS). However, you can perform this check for any output condition by using the procedure described in Moretti and Baker (2008) and provided in the Excel file given in Moretti et al. (in preparation). Provided saturation with a S-bearing phase, you can use these conditions as a starting point for further calculations of simple degassing by using CHOSETTO.exe.

[FUTURE DEVELOPMENTS] CHOSETTO is based on data available in the literature until 2006 (H<sub>2</sub>O-CO<sub>2</sub> module) and 2005 (Sulfur modules and iron redox). New calibration and updates will be made available as soon as possible.

## **PAPERS TO WHICH CREDIT MUST BE GIVEN BY CHOSETTO USERS**

*For solubility and degassing and CHOSETTO building:*

P1) Moretti R., Papale P. and Ottonello G. (2003). A model for the saturation of C-H-O-S fluids in silicate melts. in: Oppenheimer C. Pyle D.M., Barclay J. (eds.) Volcanic Degassing, Geol. Soc. London Spec. Publ., 213, 81-101.

P2) Moretti R. and Papale P. (2004). On the oxidation state and volatile behavior in multicomponent gas-melt equilibria. Chemical Geology, 213, 265-280.

*For the core equations about iron redox please cite P2) and*

P3) Ottonello G., Moretti R., Marini L. and Vetuschi Zuccolini M. (2001). Oxidation state of iron in silicate glasses and melts: a thermochemical model. Chemical Geology, 174, 157-179.

P4) Moretti R. (2005). Polymerisation, basicity, oxidation state and their role in ionic modelling of silicate melts. *Annals of Geophysics*, 48, 4/5, 583-608.

*For the core equations about sulfur redox:*

P5) Moretti R. and Ottonello G. (2003a). A polymeric approach to the sulfide capacity of silicate slags and melts. *Metallurgical and Materials Transactions B* 34B, 399-410

P6) Moretti R. and Ottonello G.. (2005). Solubility and speciation of sulfur in silicate melts: the Conjugated-Toop-Samis-Flood-Grjotheim (CTSFG) model. *Geochimica et Cosmochimica Acta*. 69, 801-823.

*For the H<sub>2</sub>O-CO<sub>2</sub> (Solwcad) degassing module in CHOSETTO*

P7) Papale P., Moretti R., Barbato D. (2006). The compositional dependence of the saturation surface of H<sub>2</sub>O+CO<sub>2</sub> fluids in silicate melts. *Chemical Geology*, 229, 78-95.

*For the Gas Equation of State (EoS) in CHOSETTO*

P8) Belonoshko, A. B., Shi, P., and Saxena, S. K. (1992). SUPERFLUID: a FORTRAN-77 program for calculation of Gibbs free energy and volume of CHONS-Ar mixtures. *Computers & Geosciences*, 18(9), 1267-1269.

#### **OTHER USEFUL REFERENCES RELATED TO CHOSETTO EQUATIONS, THEORY AND DEVELOPMENT (in chronological order)**

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- Ottonello G. and Moretti R. (2004). Lux-Flood basicity of binary silicate melts. *Journal of Physics and Chemistry of Solids*, 65, 1609-1614.
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- Moretti R., Neuville D.R., Le Losq C. (2014) The amphoteric behavior of water in silicate melts from the point of view of their ionic-polymeric constitution., *Chemical Geology*, 367, 23-33,
- Moretti R., and Ottonello G. (In Press) Silicate melt thermochemistry and the redox state of magmas. *Reviews in Mineralogy and Geochemistry*
- Papale P. Moretti R. and Paonita A. (In Press) Thermodynamics of multi-component gas-melt equilibrium in magmas: Theory, models, and applications. *Reviews in Mineralogy and Geochemistry*
- Moretti R. (2021) Ionic syntax and equilibrium approach to redox exchanges in melts: basic concepts and the case of iron and sulfur in degassing magmas. In *Magma Redox Geochemistry* (Moretti R., Neuville D.R., eds.), *Geophysical Monograph* 266, 117-138, American Geophysical Union, John Wiley & Sons, Inc. DOI: 10.1002/9781119473206.ch6.

#### **ARTICLES IN WHICH EARLIER VERSIONS OF CHOSETTO WERE ADOPTED TO STUDY VOLCANIC DEGASSING AND PLUMBING SYSTEMS (in chronological order)**

- Aiuppa A., Moretti R., Federico C., Giudice G., Guerrieri S., Liuzzo M., Papale P., Shinohara H., and Valenza M. (2007). Forecasting Etna eruptions by real-time observation of volcanic gas composition. *Geology*, 35, 1115-1118.
- Mangiacapra A., Moretti R., Rutherford M., Civetta L., Orsi G., Papale P. (2008). The deep magmatic system of the Campi Flegrei caldera (Italy). *Geophysical Research Letters*, 35, L21304
- Aiuppa A., Federico C., Giudice G., Giuffrida G., Guida R., Guerrieri S., Liuzzo M., Moretti R. and Papale P. (2009). The 2007 eruption of Stromboli volcano: insights from real-time measurement of the volcanic gas plume CO<sub>2</sub>/SO<sub>2</sub> ratio. *Journal of Volcanology and Geothermal Research*. 189, 221-230
- Edmonds M., Aiuppa A., Humphreys M., Moretti R., Giudice G., Martin R., Herd R.A., Christopher T. (2010). Excess volatiles supplied by mingling of mafic magma at an andesitic arc volcano. *Geophysics, Geochemistry, Geosystems*, Q04005.
- Aiuppa A., Bertagnini A., Métrich N., Moretti R., Di Muro A., Liuzzo M. and Tamburello G. (2010) A degassing model for Stromboli volcano. *Earth and Planetary Science Letters*, 295 (2010) 195–204.
- Pino N.A., Moretti R., Allard P. and Boschi E. (2011) Seismic precursors of a basaltic paroxysmal explosion track deep gas slug upraise. *Journal of Geophysical Research-Solid Earth*, 116, 16, B02312.
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- Aiuppa A., Shinohara H., Tamburello G., Giudice G., Liuzzo M., Moretti R. (2011) Hydrogen in the gas plume of an open-vent volcano (Mt. Etna, Italy). *Journal of Geophysical Research – Solid Earth*, 116, B10204, doi:10.1029/2011JB008461
- Moretti R., Arienzo I., Civetta L., Orsi G, D’Antonio M. (2013a) The deep plumbing system of the Ischia island: a physico-chemical window on the fluid-saturated and CO<sub>2</sub>-sustained Neapolitan volcanism (Southern Italy). *Journal of Petrology*, 54, 951-984
- Moretti R., Arienzo I., Civetta L., Orsi G., Papale P. (2013b) Multiple magma degassing sources at an explosive volcano. *Earth and Planetary Sciences Letters*, 367, 95-104
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- Aiuppa A., Lo Coco E., Liuzzo M., Giudice G., Giuffrida G., Moretti R. (2016). Terminal Strombolian activity at Etna’s central craters during summer 2012: The most CO<sub>2</sub>-rich volcanic gas ever recorded at Mount Etna. *Geochemical Journal*, 50, doi:10.2343/geochemj.2.0395
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- Barsanti M., Papale P., Barbato D., Moretti R., Hauri E. Boschi E., Longo A. (2009). Heterogeneous large total CO<sub>2</sub> abundance in the shallow magmatic system of Kilauea volcano, Hawaii. Journal of Geophysical Research-Solid Earth, 114, B12201, doi:10.1029/2008JB006187