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PySulfSat: An Open-Source Python3 Tool for modelling sulfide and sulfate saturation.

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Please feel free to get in contact with penny_wieser@berkeley.edu with any suggestions. Please, contact me with anything that isn't clear to you, or anything you want added (chances are, if you are confused, or want a model, you are not the only one!).

We will also be adding videos to the YouTube channel:

https://www.youtube.com/channel/UC3J8Lj6Yv_87nvdjjKKcG0g

And there are lots of examples on the Read The Docs page:

https://pysulfsat.readthedocs.io/en/latest/index.html?utm_source=Read+The+Docs

PySulfSat: An Open-Source Python3 Tool for modelling sulfide and sulfate saturation

Penny E. Wieser*[†], Matthew Gleeson[‡]

Abstract

We present PySulfSat, an Open-Source Python3 tool for modeling sulfide and anhydrite saturation in magmas. PySulfSat supports a variety of data types (spreadsheets, Petrolog3 outputs, MELTS tbl files). PySulfSat can be used with alphaMELTS for Python infrastructure to track sulfur solubility during fractional crystallization within a single Jupyter Notebook. PySulfSat allows far more customization of calculations than existing tools. For example, the SCSS^{2-} could be calculated with one model using the sulfide composition from a parameterization released with a different SCSS^{2-} model. There are also functions for calculating the proportion of S^{6+}/S$_{Tot}$, allowing modeled SCSS and SCAS values to be converted into total S solubility to compare to natural data. We also contain functions for modeling mantle melting in the presence of sulfides using a variety of SCSS and K$_D$ models. Extensive documentation and worked examples are available at ReadTheDocs (`https://bit.ly/PySulfSatRTD`) along with narrated YouTube videos (`https://bit.ly/PySulfSatYouTube`).

1 Introduction

Modeling the solubility of sulfur in a silicate melt provides vital insights into the evolution of sulfur and other S-loving (chalcophile) elements during mantle melting, and crustal processes such as fractional crystallization and crustal contamination (Ding and Dasgupta [2018]; Wieser et al. [2020]; Reekie et al. [2019]; Virtanen et al. [2022]; Muth and Wallace [2022]; Virtanen et al. [2022]; Wieser and Jenner [2021]). Modeling the removal of sulfides and sulfate phases is particularly vital to understand the formation of economical deposits of chalcophile elements, as well as the sulfur and metal flux emitted to the atmosphere during volcanic eruptions (Mason et al. [2021]; Edmonds et al. [2018]; Wieser et al. [2020]). A number of different models have been proposed over the years to calculate the sulfide content at sulfide saturation (SCSS^{2-}), which describes the maximum amount of sulfide (S^{2-}) that can dissolve in a silicate melt before it becomes saturated in a sulfide phase (e.g., Smythe et al. [2017]; O'Neill [2021]; Fortin et al. [2015]; Li and Ripley [2009]). Numerous models also exist to quantify the sulfate content at anhydrite saturation (SCAS), which describes the amount of sulfate (S^{6+}) that can dissolve in a silicate melt before it becomes saturated in anhydrite (e.g., Chowdhury and Dasgupta [2019], Zajacz and Tsay [2019], Masotta and Keppler [2015], Baker and Moretti [2011], Li and Ripley [2009]). In many magmas with intermediate oxygen fugacity (e.g. in volcanic arcs), S is present as a mixture of S^{2-} and S^{6+} species. O'Neill and Mavrogenes [2022], Smythe et al. [2017], and Jugo et al. [2010] produce models to quantify the proportion of these two species as a function of melt redox. These speciation models can be used alongside SCSS^{2-} and SCAS^{6+} calculations to obtain the total amount of S that is dissolved in the melt (to compare to measured S contents in volcanic systems).

1.1 Previously-available tools

At the moment, SCSS^{2-} and SCAS^{6+} calculations are performed in spreadsheets accompanying each publication (e.g., Smythe et al. [2017]; O'Neill [2021]; Fortin et al. [2015]). These spreadsheets require users to paste in their melt compositions with oxides in a specific order, and the order differs between spreadsheets. This makes it difficult to quickly compare the outputs from different models. Many of these calculators also have a limited number of rows that can perform calculations (e.g., N=50 for Smythe et al. [2017], N=194 for O'Neill [2021]), making it difficult to apply them to thousands of compositions, or fractional crystallization models with a small temperature step. These spreadsheets can also contain errors, or may not match the equations

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given in the paper, resulting in problems with reproducibility. To compare different models, the outputs must be extracted from each spreadsheet, and compiled into a single format and location for plotting. There are also tools for which no published spreadsheets exist (e.g. Blanchard et al. [2021]), requiring users to contact the author team, or individually interpret the equations (which often contain typos, or ambiguities, particularly regarding which units to use).

The most recent SCSS^{2-} models have a term accounting for the composition of the sulfide (Smythe et al. [2017], O'Neill [2021], Li and Zhang [2022], Blanchard et al. [2021], Liu et al. [2021]), because melts in equilibrium with a sulfide containing Ni and Cu have a substantially lower SCSS compared with melts in equilibrium with pure Fe-S sulfides. However, the spreadsheets for these different models use a variety of approaches to account for the composition of the sulfide, making it hard to directly compare model outputs. The Smythe et al. [2017] Excel workbook has two sheets; one is designed for users to enter a sulfide composition in wt %, while the other sheet calculates a sulfide composition using partition coefficients from Kiseeva and Wood [2015] and an estimate of the Ni and Cu content in the melt. In contrast, the spreadsheet of O'Neill [2021] calculates the Fe/(Fe+Cu+Ni) content of the sulfide using a simple regression based on the FeO$_t$, Ni and Cu content of the melt (calibrated on MORB), although the user can overwrite this and paste in a fixed value of Fe/(Fe+Cu+Ni). The spreadsheets of Li and Zhang [2022] and Liu et al. [2021] require users to input an estimate of Fe/(Fe+Cu+Ni). To be able to robustly compare the calculated SCSS^{2-} using these three different models, it would be optimal to use the same routine for calculating sulfide composition, to remove the influence of different calculated sulfide compositions during model comparisons. At the moment, this would require substantial tweaking of spreadsheets by each user.

1.2 PySulfSat: An Open-source approach

The tedium associated with performing SCSS^{2-} and SCAS^{6+} calculations in existing spreadsheets, and difficulties associated with comparing models, motivated the production of PySulfSat, an Open-Source package written in the popular programming language Python3. PySulfSat is designed to be accessible to people with no coding experience. All users must do is download a python installation (e.g. through Anaconda), and then PySulfSat can be installed onto any computer through PyPI using the simple command in the command line:

```
pip install PySulfSat
```

Or, if installation is performed in a Jupyter notebook, an explanation mark is simply added:

```
!pip install PySulfSat
```

Once it is installed on a given computer, PySulfSat must be loaded into each Jupyter Notebook (or other Python environment) using any combination of letter users wish (here we use ss):

```
import PySulfSat as ss
```

Any function is then called from PySulfSat using `ss.function_name`.

In addition, we encourage users to import pandas (pandas development team [2020]), NumPy (Harris et al. [2020]), and matplotlib (Hunter [2007]) at the start of each script, for ease of plotting and data manipulation after performing PySulfSat calculations:

```
import pandas as pd
import numpy as np
import matplotlib.pyplot as plt
```

We include numerous narrated worked examples on the PySulfSat YouTube channel to make this package more accessible to non coders `https://bit.ly/PySulfSatYouTube`.

Some relevant terminology for Python (and S modelling) is shown in Fig. 1.

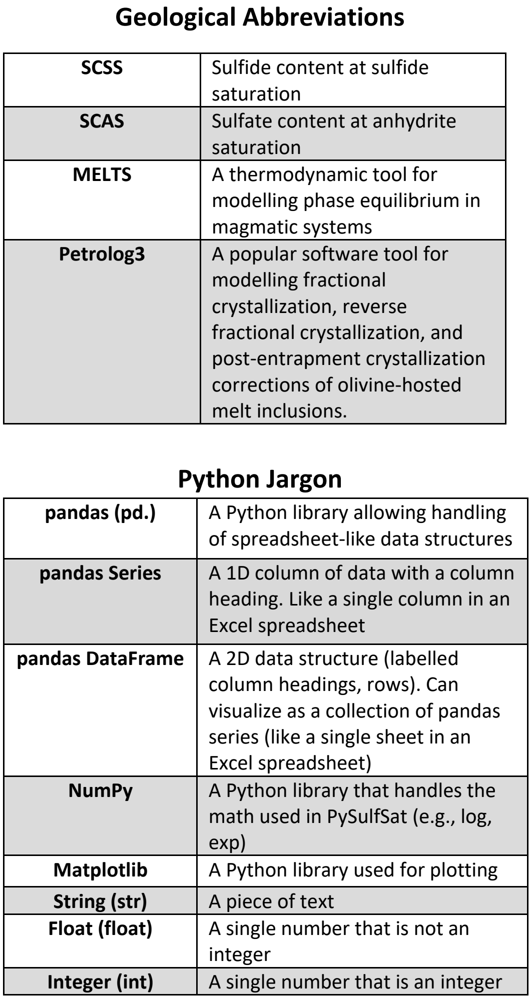
1.3 Importing data

Users can import data from any excel spreadsheet using the `import_data` function. The input spreadsheet should have the following column headings with oxide contents in wt%:

1. SiO2_Liq
2. TiO2_Liq
3. Al2O3_Liq
4. FeOt_Liq
5. MnO_Liq
6. MgO_Liq
7. CaO_Liq
8. Na2O_Liq
9. K2O_Liq

Specific models also require users to input the following parameters (Fig. 2):

1. P2O5_Liq



Geological Abbreviations

SCSS	Sulfide content at sulfide saturation
SCAS	Sulfate content at anhydrite saturation
MELTS	A thermodynamic tool for modelling phase equilibrium in magmatic systems
Petrolog3	A popular software tool for modelling fractional crystallization, reverse fractional crystallization, and post-entrapment crystallization corrections of olivine-hosted melt inclusions.

Python Jargon

pandas (pd.)	A Python library allowing handling of spreadsheet-like data structures
pandas Series	A 1D column of data with a column heading. Like a single column in an Excel spreadsheet
pandas DataFrame	A 2D data structure (labelled column headings, rows). Can visualize as a collection of pandas series (like a single sheet in an Excel spreadsheet)
NumPy	A Python library that handles the math used in PySulfSat (e.g., log, exp)
Matplotlib	A Python library used for plotting
String (str)	A piece of text
Float (float)	A single number that is not an integer
Integer (int)	A single number that is an integer

Figure 1: List of abbreviations

2. H2O_Liq
3. Fe3Fet_Liq

The `import_data` function returns a pandas dataframe (see Fig. 1). The order of the columns in the input spreadsheet doesn't matter, as columns are identified based on their column heading rather than position. If any column headings are missing in the input spreadsheet, they will be filled with zeros. Any additional columns entered by the user (e.g., temperature, pressure, sulfide composition) are appended onto the end of the outputted dataframe, for easy access for calculations. For example, the O'Neill [2021] and Smythe et al. [2017] models require the Ni and Cu content of the liquid in ppm. These can be stored in a column with any heading the user wishes (e.g. `Ni_Liq_ppm`, `Cu_Liq_ppm`), and then obtained from the outputted dataframe (df) using `df['column_name']` to input into the function of interest.

For example, to import generic data (perhaps whole-rock, matrix glass or melt inclusion compositions) from a spreadsheet named "`Liquids1.xlsx`" stored in "`Sheet3`":

```
df_out=ss.import_data(filename='Liquids1.xlsx',
sheet_name='Sheet3')
```

This function also supports specific output files from other petrological modelling programs. For example, users can load in the default spreadsheet-based output from Petrolog3.1.1.3 Danyushevsky and Plechov [2011]. Here, the Petrolog output is saved to an excel file named "`Petrolog_Model1.xlsx`":

```
df_out=ss.import_data(filename='Petrolog_Model1.xlsx',
Petrolog=True)
```

Similarly, the standard liquid ".tbl" output from MELTS (Gualda et al. [2012]; Ghiorso and Sack [1995]; Asimow and Ghiorso [1998]) can be imported:

```
df_out=ss.import_data(filename='melts-liquid.tbl',
MELTS=True)
```

In these examples, the `import_data` function has identified the appropriate column headings in each default structure, and has changed the column names into the format required by PySulfSat (e.g., converting `SiO2_melt` from Petrolog3 into `SiO2_Liq`).

2 UNITS

All temperatures should be entered in Kelvin, all pressures in kbar, and all melt oxides in wt%, apart from Ni and Cu contents in the liquid which are entered in ppm. All ratios are atomic (e.g. Fe/(Fe+Ni+Cu) in the sulfide).

2.1 Available functions

PySulfSat implements the most recent SCSS^{2-} and SCAS^{6+} models (Fig. 2). The open-source nature of PySulfSat means we anticipate continuining to add models as they are published, so users should check the 'Available Functions' tab on the ReadTheDocs page.

2.2 Calibration datasets

Many SCSS and SCAS models are empirical. Thus, it is not recommended that they are extrapolated too far beyond the compositional range of the calibration dataset. We have compiled available calibration datasets, and incorporated them into PySulfSat (see Fig. 2 for available datasets). This means that users can easily plot their melt compositions, and estimates of the pressures and temperatures of their system alongside the dataset used to calibrate each model, to assess its suitability. The function `return_cali_dataset` returns the calibration dataset for a given model. For example, to obtain the calibration dataset for the Smythe et al. [2017] SCSS model as a pandas.DataFrame:

```
df_S2017=ss.return_cali_datasets(model='S2017_SCSS')
```

One example showing a number of different models in P-T and TAS space is shown in Fig. 3).

2.3 Worked examples

Example Jupyter Notebooks showing a number of workflows are available on the ReadTheDocs page (`bit.ly/PySulfSatRTD`). This list is not exhaustive, and we anticipate that we will continue adding examples in the future:

- A notebook showing how to import different data types (e.g. measured oxide contents, Petrology3 files, and MELTS tbl outputs)
- A notebook showing how to calculate the SCSS and SCAS using a variety of models during fractional crystallization from a Petrolog3 output (Danyushevsky and Plechov [2011]). This example also shows how to calculate the trajectory of S if a sulfide phase wasn't present, and how to calculate the mass fraction of sulfide which has formed during crystallization
- Notebooks showing how to run SCSS and SCAS calculations for a MELTS fractional crystallization path calculated within the same Jupyter Notebook using PyMELTScalc (Gleeson et al. [2023]).
- Notebooks showing how to model the SCSS from a Petrolog3 path, and compare models of S contents and sulfide composition to natural melt inclusion and sulfide data from Holuhraun, Iceland (workflows presented in detail in Liu et al. [ress]).
- Notebooks showing how to calculate the proportion of S^{6+} using the models of Jugo et al. [2010], Nash et al. [2019], and O'Neill and Mavrogenes [2022].
- Notebooks showing how to perform calculations of trace element evolution during mantle melting in the presence of sulfide using various different SCSS, SCAS and K_D models.
- Notebooks showing other useful features, including calculating K_Ds using various models, converting between S isotope ratios and delta notation, and abundances of different S-bearing species.

3 SCSS^{2-} MODELS

There are a number of ways to perform SCSS calculations, with various options discussed below (and numerous worked examples available on ReadTheDocs).

3.1 Using measured sulfide compositions

The newest SCSS models (e.g., O'Neill [2021], Smythe et al. [2017], Li and Zhang [2022], Blanchard et al. [2021]) contain terms for the composition of the sulfide. In some situations, the sulfide composition may have been directly measured in the samples of interest (e.g. using Energy Dispersive Spectroscopy, Wieser et al. [2020]). In this case, the function `calculate_sulf_FeFeNiCu` can be used to convert measured elemental abundances in wt% into the atomic Fe/(Fe+Ni+Cu) ratio used by SCSS models. In some systems, the Fe/(Fe+Ni+Cu) may remain approximately constant during fractional crystallization (Wieser et al. [2020]), meaning that a fixed value for this ratio can be used for simplicity. Figure 4 shows a worked example calculating the SCSS^{2-} using the models of Smythe et al. [2017], O'Neill [2021] and Li and Zhang [2022] for Fe/(Fe+Ni+Cu)=0.65. The expected increase in S content with fractional crystallization in the absence of a S-bearing phase is also calculated using the function `crystallize_S_incomp` for comparison (black dashes), and these different S trajectories are plotted using matplotlib (where they can be compared to natural melt inclusion or quenched submarine glass data).

Reference	**Name in PySulfSat**	**Melt composition?**	**T-sens?**	**P-sens?**	**H_2O-sens?**	***Fe^{3+} sensitive?***	**Sulfide/Sulfate comp?**	**Cali dataset available?**
SCAS models								
Chowdhury & Dasgupta (2019)	“calculate_CD2019_SCAS”	✓	✓	✗	✓	✗	✗	✓
Zajacz & Tsay (2019)	“calculate_ZT2022_SCAS”	✓	✓	✗	✓	✗	✗	✓
Masotta & Keppler (2015)	“calculate_MK2015_SCAS”	✓	✓	✗	✓	✗	✗	✓
SCSS models								
Li and Zhang (2022)	“calculate_LiZhang2022_SCSS”	✓	✓	✓	✓	✓	✓	✓
Blanchard et al. (2021)	“calculate_B2021_SCSS”	✓	✓	✓	✓	✗	✓	✓
O’Neill (2021)	“calculate_O2021_SCSS”	✓	✓	✓	✗	✓	✓	
O’Neill and Mavrogenes (2022)*1	“calculate_OM2022_SCSS”	✓	✓	✓	✗	✓	✓	✓
Liu et al. (2021)	“calculate_Liu2021_SCSS”	✗	✓	✓	✓	✗	✓	✓
Smythe et al. (2017)	“calculate_S2017_SCSS”	✓	✓	✓	✗	✓	✓	✓
Fortin et al. (2015)	“calculate_F2015_SCSS”	✓	✓	✓	✓	✗	✗	✓
Sulfide composition models								
O’Neill (2021)	“Calc_ONeill”	✓	✗	✗	✗	✓		
Smythe et al. (2017) using Kiseeva et al. (2015)	“Calc_Smythe”	✓	✓	✗	✗	✓		

Calculating Proportion of S^{6+} using empirical approaches

Reference	Name in PySulfSat	Input parameters
Jugo et al. (2010)	“calculate_S6St_Jugo2010_eq10”	ΔQFM
Nash et al. (2019)	“calculate_S6St_Nash2019”	T, Fe^{3+}/Fe_T
O’Neill and Mavrogenes (2022)	“calculate_OM2022_S6St”	Melt comp, T, log(fo_2) **or** Fe3/Fe_T

Correcting $SCSS^{2-}$ and $SCAS^{6+}$ calculations for S_T

Name in PySulfSat	Input arguments
“calculate_SCSS_Total”	$SCSS^{2-}$, S^{6+}/S_T
“Calculate_SCAS_Total”	$SCAS^{6+}$, S^{2-}/S_T
“Calculate_S_Total_SCSS_SCAS”	$SCSS^{2-}$, $SCAS^{6+}$, S^{6+}/S_T, or model (’Nash’, ‘Jugo’ or ‘Kleinsasser’)

Other functions

“crystallize_S_incomp”	Calculates S left in the melt for a given F_melt, assuming S is entirely incompatible
“calculate_mass_frac_sulf”	Calculates mass fraction of sulfide removed for a fractional crystallization path where the SCSS is modelled
“convert_d34_to_3432S”	Converts $\delta^{34}S$ to $^{34}S/^{32}S$
“Lee_Wieser_sulfide_melting”	Modelling of S and chalcophile element behavoir during mantle melting.

Figure 2: Models currently available in PySulfSat. $SCAS^{6+}$ models: Chowdhury and Dasgupta [2019], Zajacz and Tsay [2019] and Masotta and Keppler [2015]. $SCSS^{2-}$ models: Li and Zhang [2022], Blanchard et al. [2021], O’Neill [2021], O’Neill and Mavrogenes [2022], Liu et al. [2021], Smythe et al. [2017] and Fortin et al. [2015]. The SCSS model of O’Neill [2021] and O’Neill and Mavrogenes [2022] are extremely similar, differing only with regard to a 7.2*Fe*Si term in 2021, and a 7.2*(Mn+Fe)*Si term in 2022. S^{6+} corrections from Jugo et al. [2010], Nash et al. [2019] and O’Neill and Mavrogenes [2022]. We suggest readers check the ReadTheDocs page for a complete list as we will add new models as they become available.

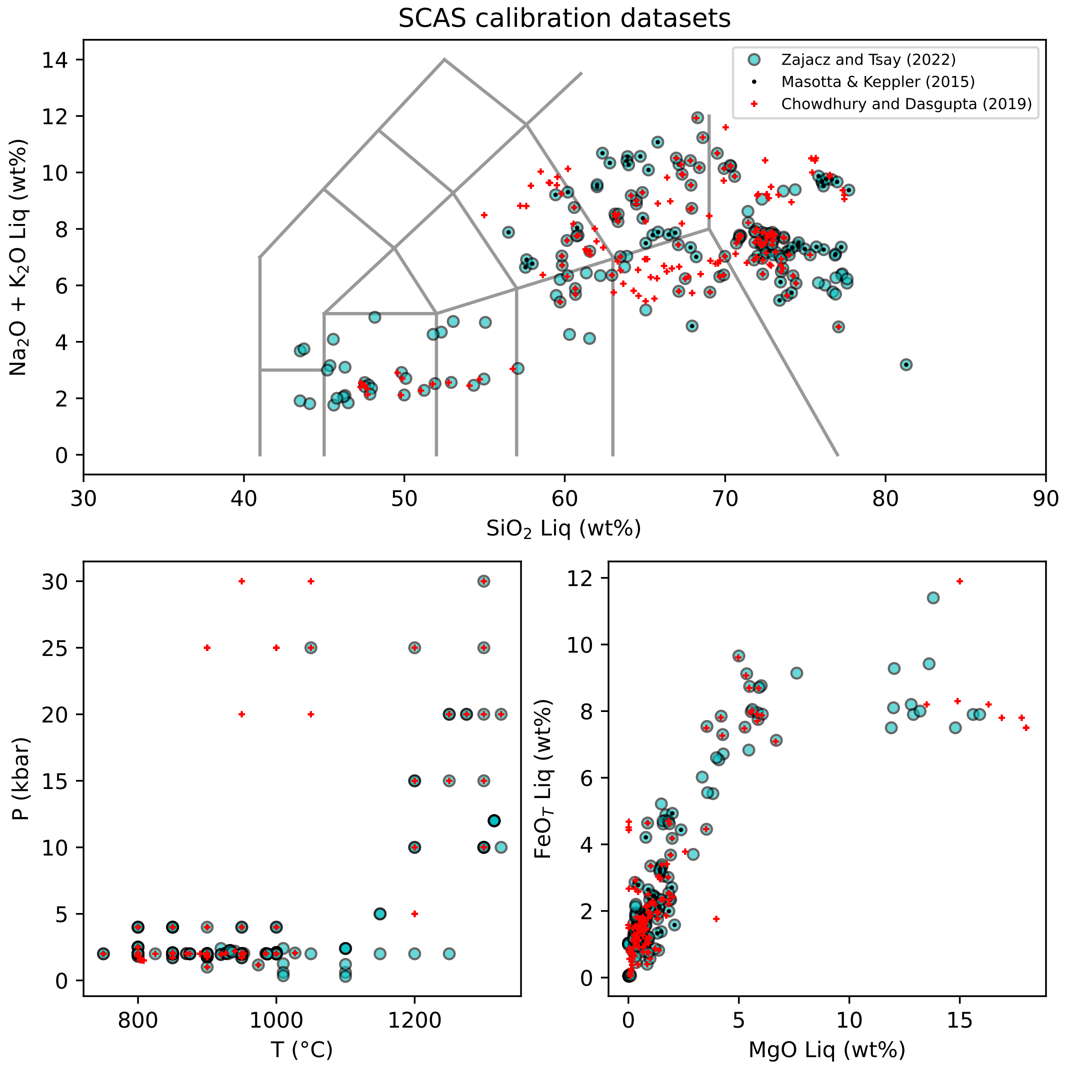
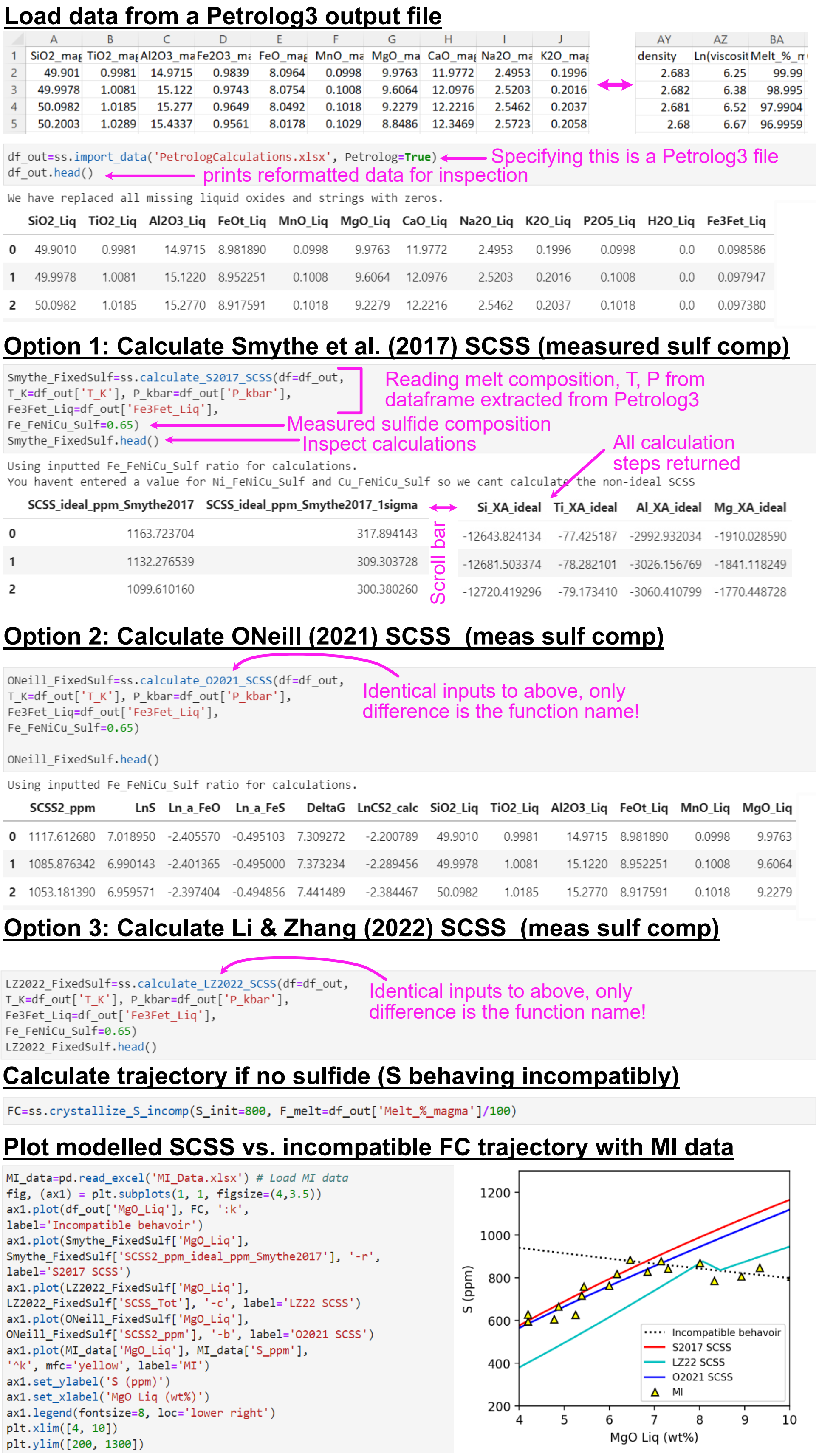


Figure 3: Plots of SCAS calibration datasets in P-T-X space. An example notebook to produce these plots, and overlay user data, is available at ReadTheDocs. Similar plots can easily be made for SCSS models.



Load data from a Petrolog3 output file

	A	B	C	D	E	F	G	H	I	J
1	SiO2_mag	TiO2_mag	Al2O3_ma	Fe2O3_ma	FeO_mag	MnO_ma	MgO_ma	CaO_mag	Na2O_ma	K2O_mag
2	49.901	0.9981	14.9715	0.9839	8.0964	0.0998	9.9763	11.9772	2.4953	0.1996
3	49.9978	1.0081	15.122	0.9743	8.0754	0.1008	9.6064	12.0976	2.5203	0.2016
4	50.0982	1.0185	15.277	0.9649	8.0492	0.1018	9.2279	12.2216	2.5462	0.2037
5	50.2003	1.0289	15.4337	0.9561	8.0178	0.1029	8.8486	12.3469	2.5723	0.2058

AY	AZ	BA
density	Ln(viscosit	Melt_%_m
2.683	6.25	99.99
2.682	6.38	98.995
2.681	6.52	97.9904
2.68	6.67	96.9959

```
df_out=ss.import_data('PetrologCalculations.xlsx', Petrolog=True)
df_out.head()
```

Specifying this is a Petrolog3 file

prints reformatted data for inspection

```
We have replaced all missing liquid oxides and strings with zeros.
```

	SiO2_Liq	TiO2_Liq	Al2O3_Liq	FeOt_Liq	MnO_Liq	MgO_Liq	CaO_Liq	Na2O_Liq	K2O_Liq	P2O5_Liq	H2O_Liq	Fe3Fet_Liq
0	49.9010	0.9981	14.9715	8.981890	0.0998	9.9763	11.9772	2.4953	0.1996	0.0998	0.0	0.098586
1	49.9978	1.0081	15.1220	8.952251	0.1008	9.6064	12.0976	2.5203	0.2016	0.1008	0.0	0.097947
2	50.0982	1.0185	15.2770	8.917591	0.1018	9.2279	12.2216	2.5462	0.2037	0.1018	0.0	0.097380

Option 1: Calculate Smythe et al. (2017) SCSS (measured sulf comp)

```
Smythe_FixedSulf=ss.calculate_S2017_SCSS(df=df_out,
T_K=df_out['T_K'], P_kbar=df_out['P_kbar'],
Fe3Fet_Liq=df_out['Fe3Fet_Liq'],
Fe_FeNiCu_Sulf=0.65)
Smythe_FixedSulf.head()
```

Reading melt composition, T, P from dataframe extracted from Petrolog3

Measured sulfide composition

Inspect calculations

All calculation steps returned

```
Using inputted Fe_FeNiCu_Sulf ratio for calculations.
You havent entered a value for Ni_FeNiCu_Sulf and Cu_FeNiCu_Sulf so we cant calculate the non-ideal SCSS
```

	SCSS_ideal_ppm_Smythe2017	SCSS_ideal_ppm_Smythe2017_1sigma
0	1163.723704	317.894143
1	1132.276539	309.303728
2	1099.610160	300.380260

Scroll bar

Si_XA_ideal	Ti_XA_ideal	Al_XA_ideal	Mg_XA_ideal
-12643.824134	-77.425187	-2992.932034	-1910.028590
-12681.503374	-78.282101	-3026.156769	-1841.118249
-12720.419296	-79.173410	-3060.410799	-1770.448728

Option 2: Calculate ONeill (2021) SCSS (meas sulf comp)

```
ONeill_FixedSulf=ss.calculate_O2021_SCSS(df=df_out,
T_K=df_out['T_K'], P_kbar=df_out['P_kbar'],
Fe3Fet_Liq=df_out['Fe3Fet_Liq'],
Fe_FeNiCu_Sulf=0.65)

ONeill_FixedSulf.head()
```

Identical inputs to above, only difference is the function name!

```
Using inputted Fe_FeNiCu_Sulf ratio for calculations.
```

	SCSS2_ppm	LnS	Ln_a_FeO	Ln_a_FeS	DeltaG	LnCS2_calc	SiO2_Liq	TiO2_Liq	Al2O3_Liq	FeOt_Liq	MnO_Liq	MgO_Liq
0	1117.612680	7.018950	-2.405570	-0.495103	7.309272	-2.200789	49.9010	0.9981	14.9715	8.981890	0.0998	9.9763
1	1085.876342	6.990143	-2.401365	-0.495000	7.373234	-2.289456	49.9978	1.0081	15.1220	8.952251	0.1008	9.6064
2	1053.181390	6.959571	-2.397404	-0.494856	7.441489	-2.384467	50.0982	1.0185	15.2770	8.917591	0.1018	9.2279

Option 3: Calculate Li & Zhang (2022) SCSS (meas sulf comp)

```
LZ2022_FixedSulf=ss.calculate_LZ2022_SCSS(df=df_out,
T_K=df_out['T_K'], P_kbar=df_out['P_kbar'],
Fe3Fet_Liq=df_out['Fe3Fet_Liq'],
Fe_FeNiCu_Sulf=0.65)
LZ2022_FixedSulf.head()
```

Identical inputs to above, only difference is the function name!

Calculate trajectory if no sulfide (S behaving incompatibly)

```
FC=ss.crystallize_S_incomp(S_init=800, F_melt=df_out['Melt_%_magma']/100)
```

Plot modelled SCSS vs. incompatible FC trajectory with MI data

```
MI_data=pd.read_excel('MI_Data.xlsx') # Load MI data
fig, (ax1) = plt.subplots(1, 1, figsize=(4,3.5))
ax1.plot(df_out['MgO_Liq'], FC, ':k',
label='Incompatible behavoir')
ax1.plot(Smythe_FixedSulf['MgO_Liq'],
Smythe_FixedSulf['SCSS2_ppm_ideal_ppm_Smythe2017'], '-r',
label='S2017 SCSS')
ax1.plot(LZ2022_FixedSulf['MgO_Liq'],
LZ2022_FixedSulf['SCSS_Tot'], '-c', label='LZ22 SCSS')
ax1.plot(ONeill_FixedSulf['MgO_Liq'],
ONeill_FixedSulf['SCSS2_ppm'], '-b', label='O2021 SCSS')
ax1.plot(MI_data['MgO_Liq'], MI_data['S_ppm'],
'^k', mfc='yellow', label='MI')
ax1.set_ylabel('S (ppm)')
ax1.set_xlabel('MgO Liq (wt%)')
ax1.legend(fontsize=8, loc='lower right')
plt.xlim([4, 10])
plt.ylim([200, 1300])
```

Figure 4: Annotated worked example showing how to calculate SCSS^{2-} for a Petrolog3 fractional crystallization path using a fixed Fe/(Fe+Ni+Cu) ratio in the sulfide. Hypothetical melt inclusion data is overlain. The data initially follows the incompatible fractional crystallization trend, followed by a prominent downturn following sulfide saturation at ∼ 6-7 wt% MgO.

3.2 Calculating Sulfide Compositions

While using a measured sulfide composition is the simplest and most reliable method to perform SCSS^{2-} calculations, direct measurements of sulfide compositions do not exist in many systems. PySulfSat allows users to calculate sulfide composition from Ni and Cu contents of the liquid using the approaches implemented in the supporting spreadsheets of O'Neill [2021] and Smythe et al. [2017]. The O'Neill [2021] method is the simplest, calculating the atomic Fe/(Fe+Ni+Cu) ratio using the following empirical expression:

$$\left(\frac{Fe}{Fe+Ni+Cu}\right)_{sulf} = \frac{1}{1+0.031\frac{Ni_{Liq,\,ppm}}{FeO_{Liq,\,wt}}+0.025*\frac{Cu_{Liq,\,pp}}{FeO_{Liq,\,w}}} \quad (1)$$

Where:

$$FeO_{Liq,wt} = FeOt_{Liq,wt} \times (1 - Fe^{3+}/Fe_T) \quad (2)$$

In contrast, Smythe et al. [2017] use an iterative approach based on the partition coefficients of Cu and Ni in sulfide from Kiseeva and Wood [2015], which are sensitive to temperature, liquid FeO content, and the Ni and Cu content of the sulfide. Specifically, for a given sulfide Ni and Cu content, a partition coefficient can be calculated. Using this partition coefficient, and the Ni and Cu sulfide content, the amount of Ni and Cu expected in the melt can be calculated. Smythe et al. [2017] calculate the residual between the calculated and measured Ni and Cu contents of the melt:

$$\begin{aligned} residual = \; & (Ni_{Liq}^{Calc} - Ni_{Liq}^{Meas})^2 \\ & + (Cu_{Liq}^{Calc} - Cu_{Liq}^{Meas})^2 \end{aligned} \quad (3)$$

Using the Excel solver function, they vary the contents of Cu and Ni in the sulfide to minimise this residual. Then, the equation of Kiseeva and Wood [2015] is used to calculate the Fe content of the sulfide for these best fit Ni and Cu contents, and these 3 parameters are used to calculate the sulfide Fe/(Fe+Ni+Cu) ratio. In PySulfSat, this convergence routine is performed using the scipy optimize minimize function (Virtanen et al. [2020]). In Excel, for many compositions, the result obtained can depend slightly on the starting value of the Ni and Cu contents in the sulfide provided by the user. By default, the PySulfSat minimisation starts with initial Ni and Cu contents of 5 wt%, but these parameters can be overwritten using `Cu_Sulf_init=10` and `Ni_Sulf_init=5`. These parameters are allowed to vary between 0-30 wt%. In general, we find our python implementation of this solver method is stable and gives identical results to the Excel version for the same starting composition (and the vast majority of samples converge regardless of the starting Ni and Cu contents).

To perform SCSS calculations using models to predict sulfide compositions, a string should be entered into the function for the `Fe_FeNiCu_Sulf` argument. For example, to use the Smythe et al. [2017] SCSS^{2-} model with the O'Neill [2021] calculated sulfide composition, enter `Fe_FeNiCu_sulf='Calc_ONeill'`. Users must also specify the Cu and Ni content in the liquid. In the example below, `Ni_Liq (ppm)` and `Cu_Liq (ppm)` are columns in the loaded dataframe `df_out` containing estimated Ni and Cu contents of the melt in ppm:

```
S17_SCSS_S17_Sulf=ss.calculate_S2017_SCSS(df=df_out,
Fe_FeNiCu_Sulf="Calc_ONeill",
T_K=df_out['T_K'], P_kbar=df_out['P_kbar'],
Fe3Fet_Liq=df_out['Fe3Fet_Liq'],
Ni_Liq=df_out['Ni_Liq (ppm)'],
Cu_Liq=df_out['Cu_Liq (ppm)'])
```

Similarly, to use the O'Neill [2021] SCSS^{2-} model with the Smythe et al. [2017] calculated sulfide composition, use `Fe_FeNiCu_Sulf='Calc_Smythe'`:

```
O21_SCSS_S17_Sulf=ss.calculate_O2021_SCSS(df=df_out,
Fe_FeNiCu_Sulf="Calc_Smythe",
T_K=df_out['T_K'], P_kbar=df_out['P_kbar'],
Fe3Fet_Liq=df_out['Fe3Fet_Liq'],
Ni_Liq=df_out['Ni_Liq (ppm)'],
Cu_Liq=df_out['Cu_Liq (ppm)'])
```

3.3 H_2O-sensitivity

Unlike the SCSS^{2-} models of O'Neill [2021] and Smythe et al. [2017] which contain no term for H_2O, the SCSS^{2-} models of Fortin et al. [2015], Liu et al. [2021], Blanchard et al. [2021] and Li and Zhang [2022] are sensitive to the amount of H_2O in the liquid. By default, the SCSS^{2-} functions for each of these models (Fig. 2) use the H_2O content stored in the data loaded by the user in the column `H2O_Liq`. However, this can also be overwritten in the function itself, to allow detailed investigation of the sensitivity of calculations to melt water content. For example, to perform all calculation at 3 wt% H_2O using the Fortin et al. [2015] model:

```
F2015_3H=ss.calculate_F2015_SCSS(df=df_out,
T_K=df_out['T_K'], P_kbar=df_out['P_kbar'],
H2O_Liq=3)
```

The argument `H2O_Liq` could also be set to a pandas series (e.g., any other column in the loaded data), which would allow calculations to be performed using several different water contents (e.g., `df_out['Raman_H2O']` for Raman spectroscopy measurements vs. `df_out['SIMS_H2O']` for SIMS measurements in the same samples).

3.4 Redox sensitivity

A number of SCSS models are also sensitive to the ratio of Fe^{3+}, because they contain a term for only Fe^{2+} species in the melt (see Fig. 2). The input argument `Fe3Fet_Liq` should be supplied when using these models. If no value is entered, calculations are performed assuming Fe^{3+}=0. Alternatively, users can specify a single value in the function (e.g., `Fe3Fet_Liq=0.15`), or refer to a column in the input dataframe. Another option is to use the Python package Thermobar (Wieser et al. [2022]) to convert a log fO_2 value or buffer position into a `Fe3Fet_Liq` ratio.

3.5 Calculating sulfide proportions

The difference between the fractional crystallization trajectory and the predicted $SCSS^{2-}$ can be used to calculate the cumulative mass proportion of sulfide forming over the fractionation interval (after Kiseeva and Wood [2015]):

$$X_{Sulf} = \frac{S_{init} - F_{melt} * S_{model}}{S_{sulf}} \quad (4)$$

Where S_{init} is the initial S content at the start of the fractional crystallization sequence (F_{melt}=1), F_{melt} is the melt fraction remaining at each step, S_{model} is the modeled solubility of S^{2-} in the melt, and S_{sulf} is the S content of the sulfide (all concentrations in ppm).

In PySulfSat, this is calculated as follows for the example shown in Fig. 4:

```
S_Frac=ss.calculate_mass_frac_sulf(
S_model=ONeill_FixedSulf['SCSS2_ppm'],
S_sulf=320000, S_init=800,
F_melt=df_out['Fraction_melt']/100)
```

This calculates the amount of Sulfide formed as a mass fraction for a magma with 1000 ppm S initially, a sulfide with 32 wt%, and a melt fraction provided in a Petrolog3 file (column heading `Fraction_melt`, obtained from the column `Melt_%_magma` in the Petrolog3 file by the PySulfSat import function).

4 $SCAS^{6+}$ MODELS

In PySulfSat, $SCAS^{6+}$ calculations are performed in a very similar way to $SCSS^{2-}$ calculations. For example, to calculate $SCAS^{6+}$ for the Petrolog3 model loaded in as `df_out` using the model of Chowdhury and Dasgupta [2019]:

```
CD19_SCAS=ss.calculate_CD2019_SCAS(df=df_out,
T_K=df_out['T_K'])
```

The calculation could also be performed using the $SCAS^{6+}$ model of Zajacz and Tsay [2019]:

```
ZT22_SCAS=ss.calculate_ZT2022_SCAS(df=df_out,
T_K=df_out['T_K'])
```

As for $SCSS^{2-}$ models, these functions return the calculated $SCAS^{6+}$, all intermediate calculations, and the originally-loaded compositions. The main simplification relative to SCSS models is the fact that none of the existing SCAS models have a term for the composition of the sulfate-bearing phase, pressure, or the Fe^{3+}/Fe_T ratio (Fig. 2).

5 MAGMAS WITH A MIX OF S^{2-} AND S^{6+}

Silicate melts undergo a relatively abrupt transition in S speciation from sulfide (S^{2-}) to sulfate (S^{6+}) dominated with increasing oxygen fugacity (Fincham and Richardson [1954]; Jugo et al. [2010]; Kleinsasser et al. [2022]; Wallace and Carmichael [1994], cyan line, Fig. 5b). In systems where S^{2-} and S^{6+} are present, the calculated $SCSS^{2-}$ will underestimate the total solubility of S, because this parameter only accounts for the solubility of S^{2-} species. Similarly, in systems dominated by S^{6+} with some S^{2-}, the total solubility of S will exceed the $SCAS^{6+}$ (Jugo [2009]).

5.0.1 *Demonstrating the importance of S^{2-} and S^{6+} corrections*

To demonstrate the importance of accounting for both S^{2-} and S^{6+} species when modeling total S solubility, lets consider a melt with an $SCSS^{2-}$ of 1000 ppm, and an $SCAS^{6+}$ of 5000 ppm. Equation 10 of Jugo et al. [2010] can be used to calculate the proportion of S^{6+}/S_T as a function of ΔQFM between -1 and +3:

$$\frac{S^{6+}}{S_T} = \frac{1}{1 + 10^{2.1 - 2\Delta FMQ}} \quad (5)$$

This equation can be implemented in PySulfSat for a single ΔQFM value as follows:

```
S6St_03=ss.calculate_S6St_Jugo2010_eq10(deltaQFM=0.3)
```

To produce the cyan line on Fig. 5b, we input a linearly-spaced numpy array of 10,001 points between ΔQFM=-1 and ΔQFM=3 generated using the `np.linspace` function, and calculate S^{6+}/S_T for every value in this array (cyan line, Fig. 5b).

```
deltaQFM=np.linspace(-1, 3, 10001)
S6St=ss.calculate_S6St_Jugo2010_eq10(
deltaQFM=deltaQFM)
```

At ΔQFM=-1 (point 1 on Fig. 5b), the melt is sufficiently reduced that only S^{2-} is dissolved in meaningful quantities (S^{6+}/S_T=0.00008). Thus, the total solubility of sulfur is well approximated by the

$SCSS^{2-}$ (1000 ppm for this specific example, horizontal magenta line on Fig. 5a). For a moderately oxidized melt at ΔQFM=1, S^{6+}/S_T=0.44, so the presence of S^{6+} species substantially increases the total amount of S that is dissolved. Thus, the $SCSS^{2-}$ must be corrected to obtain the $SCSS_T$ using the equation of Jugo et al. [2010]:

$$SCSS_T = \frac{SCSS^{2-}}{1 - \frac{S^{6+}}{S_T}} \tag{6}$$

In PySulfSat this is implemented as follows:

```
SCSS_Tot=ss.calculate_SCSS_Total(SCSS=1000,
S6St_Liq=0.44)
```

The $SCSS_T$ is 1794, with 1000 ppm of S^{2-}, and 794 ppm of S^{6+} (see red and grey lines on Fig. 5b).

Similar corrections can be performed to determine the total amount of sulfur dissolved in more oxidised melts, by correcting the $SCAS^{6+}$ for the presence of S^{2-}:

$$SCAS_T = \frac{SCAS^{6+}}{1 - \frac{S^{2-}}{S_T}} \tag{7}$$

In PySulfSat this is implemented as follows:

```
SCAS_Tot=ss.calculate_SCAS_Total(SCAS=5000,
S2St_Liq=1-0.4)
```

At ΔQFM=1.4 (Point 3), S^{6+}/S_T=0.833. Using equation 6, the $SCSS_T$ is 6000 ppm, with 1000 ppm of S^{2-}, and 5000 ppm of S^{6+}. However, if ΔQFM (and therefore S^{6+}/S_T) increases slightly more, equation 6 becomes invalid, because the amount of predicted S^{6+} exceeds the $SCAS^{6+}$ (dashed magenta line, Fig. 5a). For example, at point 4 (ΔQFM=2), S^{6+}/S_T=0.988. Equation 6 would predict that the $SCSS_T$ is 80,432 ppm, with 1000 ppm of S^{2-}, and 79,432 ppm of S^{6+}. However, this much S^{6+} cannot dissolve, because the $SCAS^{6+}$ is only 5000 ppm. Similarly, using equation 7, at Point 4 (ΔQFM=2), there is a relatively minor contribution from S^{2-} (62 ppm), at Point 3, there is 1000 ppm S^{2-}, and at point 2, the amount of predicted S^{2-} greatly exceeds the $SCSS^{2-}$.

Clearly, at certain proportions of S^{6+} to S^{2-}, Equation 6 and 7 are invalid to predict the total solubility of S. For the specific $SCSS^{2-}$ and $SCAS^{6+}$ values used in this example, ΔQFM=1.4 is the oxygen fugacity where the maximum amount of S dissolves in the system, because at this ΔQFM value, the ratio of S^{6+}/S_T is optimized such that the amount of S^{2-} dissolved is equal to the $SCSS^{2-}$, and the amount of S^{6+} is equal to the $SCAS^{6+}$.

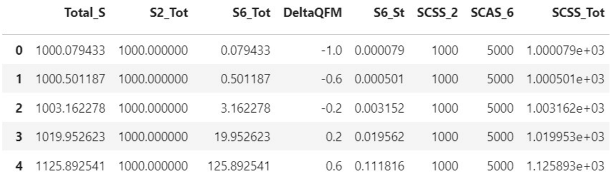
The total amount of dissolved S in ΔQFM space that does not violate the calculated $SCSS^{2-}$ and $SCAS^{6+}$ is defined by the section of the $SCSS_T$ curve where S^{6+} does not exceed the $SCAS^{6+}$ (magenta solid line, Fig. 5a), and the section of the $SCAS_T$ curve where S^{2-} doesn't exceed the $SCSS^{2-}$ (black solid line, Fig. 5a). The combined curve meeting these requirements is shown as a green line in Fig. 5b.

In PySulfSat, for any combination of $SCSS^{2-}$ and $SCAS^{6+}$ models, the total amount of S can be calculated using the function `calculate_S_Total_SCSS_SCAS`. This can be used to produce plots of changing S speciation with fO_2 (e.g., Fig. 5).

For example, using 11 equally spaced ΔQFM values between -1 and 3 (-1, -0.6, -0.2...), we can calculate the total solubility of S using the model of Jugo et al. [2010], for a fixed $SCSS^{2-}$ (1000 ppm) and $SCAS^{6+}$ value (5000 ppm):

```
deltaQFM_lin=np.linspace(-1, 3, 10)
df_S_Jugo=ss.calculate_S_Total_SCSS_SCAS(
deltaQFM=deltaQFM_lin,
SCSS=1000, SCAS=5000, model='Jugo')
```

This function returns a pandas dataframe:



	Total_S	S2_Tot	S6_Tot	DeltaQFM	S6_St	SCSS_2	SCAS_6	SCSS_Tot
0	1000.079433	1000.000000	0.079433	-1.0	0.000079	1000	5000	1.000079e+03
1	1000.501187	1000.000000	0.501187	-0.6	0.000501	1000	5000	1.000501e+03
2	1003.162278	1000.000000	3.162278	-0.2	0.003152	1000	5000	1.003162e+03
3	1019.952623	1000.000000	19.952623	0.2	0.019562	1000	5000	1.019953e+03
4	1125.892541	1000.000000	125.892541	0.6	0.111816	1000	5000	1.125893e+03

In addition to the Jugo et al. [2010] model which calculates S^{6+}/S_T simply in terms of ΔQFM, PySulfSat also contains the Nash et al. [2019] model, which parameterizes S^{6+}/S_T in terms of the ratio of Fe^{3+} to Fe^{2+} and temperature (in Kelvin):

$$log(\frac{S^{6+}}{S^{2-}}) = 8log(\frac{Fe^{3+}}{Fe^{2+}}) + \frac{8.7436 \times 10^6}{T^2} - \frac{27703}{T} + 20.273 \tag{8}$$

To calculate S^{6+}/S_T using this model, the temperature in Kelvin and the ratio of Fe^{3+}/Fe_T must be input:

```
Calc_Nash_S6=ss.calculate_S6St_Nash2019(
T_K=df_out['T_K'], Fe3Fet_Liq=df_out['Fe3Fet_Liq'])
```

When calculating the Total S content, simply specify `model='Nash'` rather than `model='Jugo'` in the function `calculate_S_Total_SCSS_SCAS`:

```
deltaQFM_lin=np.linspace(-1, 3, 11)
df_S_Nash=ss.calculate_S_Total_SCSS_SCAS(
deltaQFM=deltaQFM_lin,
SCSS=1000, SCAS=5000,
model='Nash', T_K=df_out['T_K'],
Fe3Fet_Liq=df_out['Fe3Fet_Liq'])
```

Kleinsasser et al. [2022] note that the transition predicted by models primarily calibrated on mafic melts (e.g., Nash et al. [2019]; Jugo et al. [2010]) is not a good match for dacitic melt compositions, where the transition occurs at higher fO_2 values

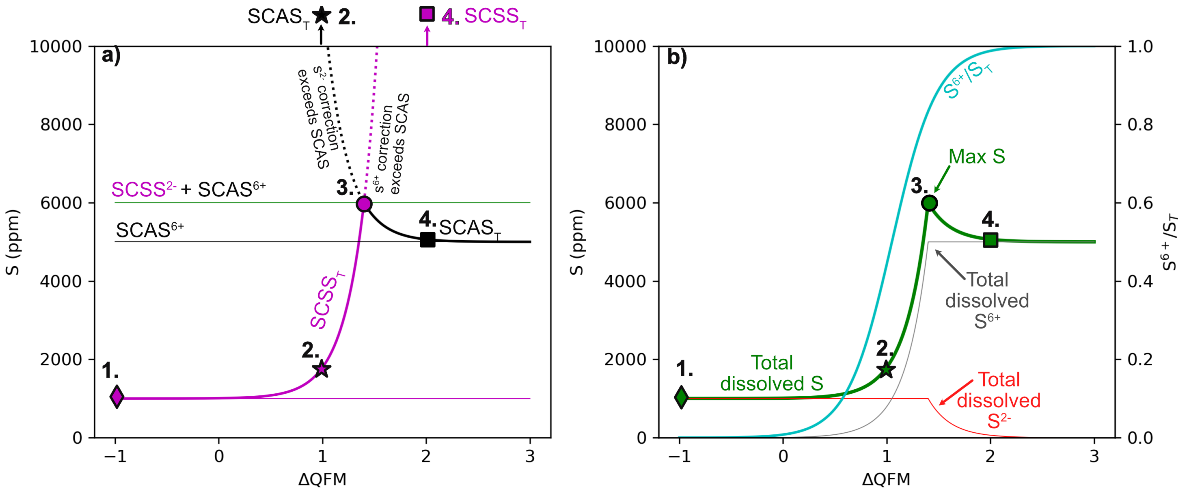


Figure 5: Calculating the total amount of dissolved S by applying corrections for the presence of both S species using the model of Jugo et al. [2010] in the function `calculate_S_Total_SCSS_SCAS`. These graphs were drawn for SCSS^{2-}=1000 ppm and SCAS^{6+}=5000 ppm, although these numbers could be calculated using any SCSS and SCAS model in PySulfSat.

(ΔQFM=+1.81 ±0.56). They provide two expressions for correcting the SCSS^{2-} and SCAS^{6+}:

$$SCSS_T^{dacitic} = SCSS^{2-} * (1 - 10^{2\Delta QFM - 3.05}) \qquad (9)$$
$$SCAS_T^{dacitic} = SCAS^{6+} * (1 - e^{1.26 - 2\Delta QFM})$$

This parameterization can also be used in PySulfSat, by specifying `model='Kleinsasser'`:

```
deltaQFM_lin=np.linspace(-1, 3, 11)
df_S_Klein=ss.calculate_S_Total_SCSS_SCAS(
deltaQFM=deltaQFM_lin,
SCSS=1000, SCAS=5000,
model='Kleinsasser')
```

5.0.2 *Calculating S^{6+}/S_T from the Sulfate and Sulfide capacity*

In addition to the methods described above where the proportion of S species is estimated from oxygen fugacity or Fe^{3+}/Fe$_T$, the ratio of S^{6+}/S$_T$ can also be calculated using the method of O'Neill and Mavrogenes [2022]. This approach calculates the sulfide capacity ($C_{S^{2-}}$) using the parameterization of O'Neill [2021], and the sulfate capacity ($C_{S^{6+}}$) using O'Neill and Mavrogenes [2022]. The equilibrium constant for the gas-phase equilibrium, lnK, is then calculated using T in Kelvin:

$$ln(K) = -55921/T + 25.07 - 0.6465 * ln(T) \qquad (10)$$

These values are then used to calculate S^{6+}/S^{2-}, which can be easily converted into a S^{6+}/S$_T$ ratio:

$$ln(\frac{S^{6+}}{S^{2-}}) = ln(C_{S^{6+}}) - ln(K) - ln(C_{S^{2-}}) + 2ln(10) \times logfO_2 \qquad (11)$$

And:

$$\frac{S^{6+}}{S^{2-}} = 1 - \frac{1}{e^{ln(\frac{S^{6+}}{S^{2-}})}} \qquad (12)$$

Their supporting spreadsheet also provides an option to input Fe^{3+}/Fe$_T$ ratio instead of a value for log$f$O$_2$. The spreadsheet uses this ratio to calculate ΔQFM using the following equation:

$$\Delta QFM = 4log(\frac{\frac{Fe^{3+}}{Fe_T}}{1 - \frac{Fe^{3+}}{Fe_T}}) + 1.36 - 2 * X_{Na} - 3.7X_K - 2.4X_{Ca} \qquad (13)$$

Where X_{Na}, X_K and X_{Ca} are the cation fractions of Na, K and Ca in the melt. This ΔQFM value is then converted into log$f$O$_2$ using the following equation:

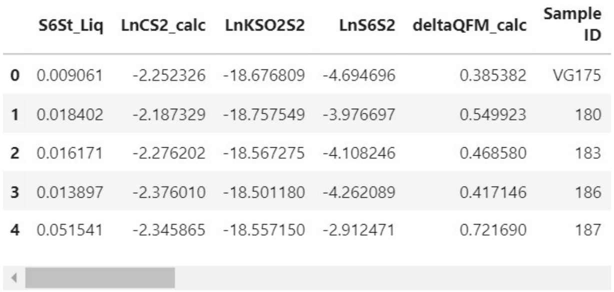
$$logfO_2 = \Delta QFM - 25050/T + 8.58 \qquad (14)$$

Where T is in Kelvin.

These equations are all implemented in PySulfSat through the function `calculate_OM2022_S6St`. For example, to perform calculations for loaded data stored in `df_out` with a column for `Fe3Fet_Liq`:

```
Calc_OM2022=ss.calculate_OM2022_S6St(df=df_out,
T_K=Liqs['T_K'], Fe3Fet_Liq=Liqs['Fe3Fet_Liq'])
```

Which returns a pandas dataframe:



	S6St_Liq	LnCS2_calc	LnKSO2S2	LnS6S2	deltaQFM_calc	Sample ID
0	0.009061	-2.252326	-18.676809	-4.694696	0.385382	VG175
1	0.018402	-2.187329	-18.757549	-3.976697	0.549923	180
2	0.016171	-2.276202	-18.567275	-4.108246	0.468580	183
3	0.013897	-2.376010	-18.501180	-4.262089	0.417146	186
4	0.051541	-2.345865	-18.557150	-2.912471	0.721690	187

Alternatively, users can enter a logfO_2 value:

```
Calc_OM2022=ss.calculate_OM2022_S6St(df=df_out,
T_K=Liqs['T_K'], logfo2=Liqs['logfo2'])
```

Boulliung and Wood [2022] also publish an equation to calculate log $C_{S^{6+}}$. While related to the ln $C_{S^{6+}}$ value of O'Neill and Mavrogenes [2022], this is not simply a log-ln conversion. Instead, Boulliung and Wood [2022] express their S content in wt percent, rather than ppm, and parameterize a different side of the equilibrium. These values can be converted from one form to another (see ReadTheDocs for a derivation). In PySulfSat, the function `calculate_BW2022_CS6` returns a dataframe for columns named `'LogCS6_calc_BW22_format'` which uses the Boulliung and Wood [2022] format, and `'LnCS6_calc_OM22_format'` which uses the format of O'Neill and Mavrogenes [2022]. This allows direct comparison between models. We also include the function `calculate_BW2022_OM2022_S6St` to calculate S^{6+}/S_T using $C_{S^{6+}}$ from Boulliung and Wood [2022] and $C_{S^{2-}}$ from O'Neill [2021].

5.0.3 *Calculations for natural samples*

When calculating the total solubility of S in natural systems, is it safest to use the function `calculate_S_Total_SCSS_SCAS` in any system with non-negligable quantities of both S species. While the functions `calculate_SCSS_Total` and `calculate_SCAS_Total` can certainly be used, it is safest to use the combined function, to ensure that the correction has not exceeded the solubility of either species. If the system is S^{2-} dominated like Hawai'i where you are unlikely to exceed the SCAS, it may be simpler to just select a SCAS value like 5000 ppm.

When comparing measured S contents to total S solubility obtained from SCSS and SCAS models, it is most reliable to use measured S^{6+}/S_T ratios (e.g., using XANES, Lerner et al. [2021]). In this ideal scenario, users can enter the measured ratio directly in the `calculate_S_Total_SCSS_SCAS` function. For example, after calculating the SCSS using Smythe et al. [2017] (saved in df=S2017) and the SCAS using Zajacz and Tsay [2019] (saved in df=Z2019), the total amount of dissolved S can be calculated using a fixed S^{6+}/S_T ratio of 0.2:

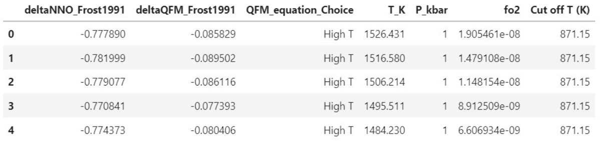
```
Tot_S_S17_Z19=ss.calculate_S_Total_SCSS_SCAS(
SCSS=S2017['SCSS_ideal_ppm_Smythe2017'],
SCAS=Z2019['SCAS6_ppm'],
S6St_Liq=0.2)
```

Alternatively, it is more common that Fe^{3+}/Fe_T has been constrained using XANES. Using the Nash et al. [2019] correction, this Fe^{3+}/Fe_T ratio can be entered directly:

```
Tot_S_S17_Z19_Nash=ss.calculate_S_Total_SCSS_SCAS(
SCSS=S2017['SCSS_ideal_ppm_Smythe2017'],
SCAS=Z2019['SCAS6_ppm'],
Fe3Fet_Liq=0.15, model='Nash')
```

To use the Jugo et al. [2010] correction, Fe^{3+}/Fe_T must be converted into fO_2. The python package Thermobar (Wieser et al. [2022]) can be used to perform such a conversion. For example, the Petrolog3 output in figure 4 has a column for the log of the fO_2 value, the temperature and the pressure.

```
!pip install Thermobar
import Thermobar as pt
Buffer_calc=pt.convert_fo2_to_buffer(
fo2=10**df_out['Lg(fO2)'],
T_K=df_out['T_K'],  P_kbar=df_out['P_kbar'])
```



```
   deltaNNO_Frost1991  deltaQFM_Frost1991  QFM_equation_Choice       T_K  P_kbar           fo2  Cut off T (K)
0           -0.777890           -0.085829               High T  1526.431       1  1.905461e-08         871.15
1           -0.781999           -0.089502               High T  1516.580       1  1.479108e-08         871.15
2           -0.779077           -0.086116               High T  1506.214       1  1.148154e-08         871.15
3           -0.770841           -0.077393               High T  1495.511       1  8.912509e-09         871.15
4           -0.774373           -0.080406               High T  1484.230       1  6.606934e-09         871.15
```

The different buffers stored in the `Buffer_calc` dataframe can then be input into the PySulfSat function:

```
ss.calculate_S_Total_SCSS_SCAS(
deltaQFM=Buffer_calc['deltaQFM_Frost1991'],
SCSS=S2017['SCSS_ideal_ppm_Smythe2017'],
SCAS=Z2019['SCAS6_ppm'],
T_K=df_out['T_K'],
model='Jugo')
```

Alternatively, if you have an estimate of fO_2, or Fe^{3+}/Fe_T, you can use the O'Neill and Mavrogenes [2022] method:

```
ss.calculate_S_Total_SCSS_SCAS(
logfo2=df_out['Lg(fO2)'],
SCSS=S2017['SCSS_ideal_ppm_Smythe2017'],
SCAS=Z2019['SCAS6_ppm'],
T_K=df_out['T_K'],
model='OM2022')
```

6 INTEGRATION WITH MELTS

While PySulfSat can load the results from a MELTS calculation as a .tbl file, recent advances in the MELTS computing infrastructure means that MELTS fractional crystallization calculations can be performed directly in Python in the same Jupyter Notebook as PySulfSat calculations. There are currently two options for performing MELTS python calculations; Thermoengine (Johnson et al. [2022]) and alphaMELTS for Python (Antoshechkina and Ghiorso [2018]). Here, we make use of the PyMELTScalc python package (see https://github.com/gleesonm1/pyMELTScalc), which provides inbuilt functions for fractional crystallizing using alphaMELTS for Python, and returns output structures consistent with the required inputs for

PySulfSat. The alphaMELTS for Python form of MELTS is easier to install on Windows than Thermoengine at present. After installing PyMELTScalc (see example on ReadTheDocs), this package must be imported into the notebook:

```
import PyMELTScalc as M
```

After loading data using the `ss.import_data` function as `df_out`, a specific melt composition can be selected as a starting composition (here, we select the first row):

```
sample=df_out.iloc[0]
```

Then, a MELTS fractional model can be initiated at a single pressure using the `multi_path` function:

```
MELTS_FC=M.multi_path(
model="MELTSv1.0.2",
comp = sample.to_dict(),
P_bar = 1000,
find_liquidus = True,
T_end_C = 750,
dt_C = 5,
Fe3Fet_Liq=0.1,
Frac_solid = True,
Frac_fluid = True)
```

This runs a fractional crystallization model at 1000 bars (P_bar), starting at the wet liquidus (`find_liquidus=True`), and runs until 700 C (T_end_C). If the MELTS calculation doesn't converge after 100 quadratic minimisation attempts, the simulation may end at a higher temperature. The temperature step is 5 C (dt_C), the initial `Fe3Fet_Liq` ratio is set at 0.1, and both fluids and solids are fractionated.

This `multi_path` function outputs a dictionary containing a series of dataframes. There is a dataframe for each phase, but most relevant for this work, there is also a dataframe named 'All' which contains the relevant outputs stitched together. This combined dataframe can be outputted using its key:

```
MELTS=MELTS_FC['All']
```

The dataframe MELTS contains system properties (T, P, enthalpy, entropy, volume), and the composition of each phase with the phase name as an underscore (e.g. `SiO2_Liq`, `SiO2_Plag` etc.). This dataframe can be fed directly into the PySulfSat code (here using the model of Li and Zhang [2022] for a measured sulfide composition):

```
LiZhang22=ss.calculate_LZ2022_SCSS(df=MELTS,
T_K=MELTS['T_C']+273.15,
P_kbar=MELTS['P_bar']/1000,
H2O_Liq=MELTS['H2O_Liq'],
Fe_FeNiCu_Sulf=0.6,
Fe3Fet_Liq=MELTS['Fe3Fet_Liq'])
```

PyMELTScalc can also be used to investigate a wide range of different fractional crystallization paths using parallel processing for computational efficiency, with hundreds to thousands of different fractional paths initiated with a single function call. For example, coupling of PyMELTScalc and PySulfSat would allow users to investigate S behavior during fractional crystallization for a single melt or range of melt compositions over a wide variety of different starting pressure, oxygen fugacities, and melt water contents. Fig. 6 shows the SCSS^{2-} calculated for fractional crystallization models run at 4 different pressures from a single call to the PyMELTScalc `multi_path` function. PyMELTScalc can run calculations at a redox buffer or unbuffered, so calculations can be implemented with the various options for the treatment of S^{6+} to investigate changes in S speciation during fractional crystallization.

7 MANTLE MELTING CALCULATIONS

Modelling the concentrations of S, Cu and other chalcophile elements during mantle melting is complicated by the fact that these elements are held in silicate minerals and mantle sulfides. Because mantle melts contain high S contents, the mantle becomes more and more depleted in sulfide during progressive melting until the sulfide phase is eventually exhausted (Wieser et al. [2020], Ding and Dasgupta [2018], Lee et al. [2012]). Exhaustion of sulfide in the mantle residue drives a large change in the bulk partition coefficient of chalcophile elements during the melting interval.

Lee et al. [2012] provide an Excel spreadsheet for calculating the concentration of Cu during near-fractional melting. This model removes small batch melts, updating the composition of the remaining mantle residue before the next melting step proceeds. The equation for batch melting is as follows: b

$$\frac{C_{melt}}{C_{source}} = \frac{1}{D_0 + F(1-P)} \quad (15)$$

Where C$_{melt}$ is the concentration in the melt, C$_{source}$ is the concentration in the mantle source, D$_0$ is the bulk partition coefficient (sulfide+silicate) at the start of that melting step, F is the degree of melt produced in that melt step, and P is the bulk partition coefficient weighted for the proportion that each component enters the melt. For simplicity, Lee et al. [2012] assume that D$_0$=P (e.g. sulfide and silicate minerals melt at the same rate). Wieser et al. [2020] update this model to account for non-modal melting behavior, accounting for the fact that the sulfide preferentially melts, so contributes more to the partition coefficient of highly chalcophile elements such as Cu. It should be noted that at a small

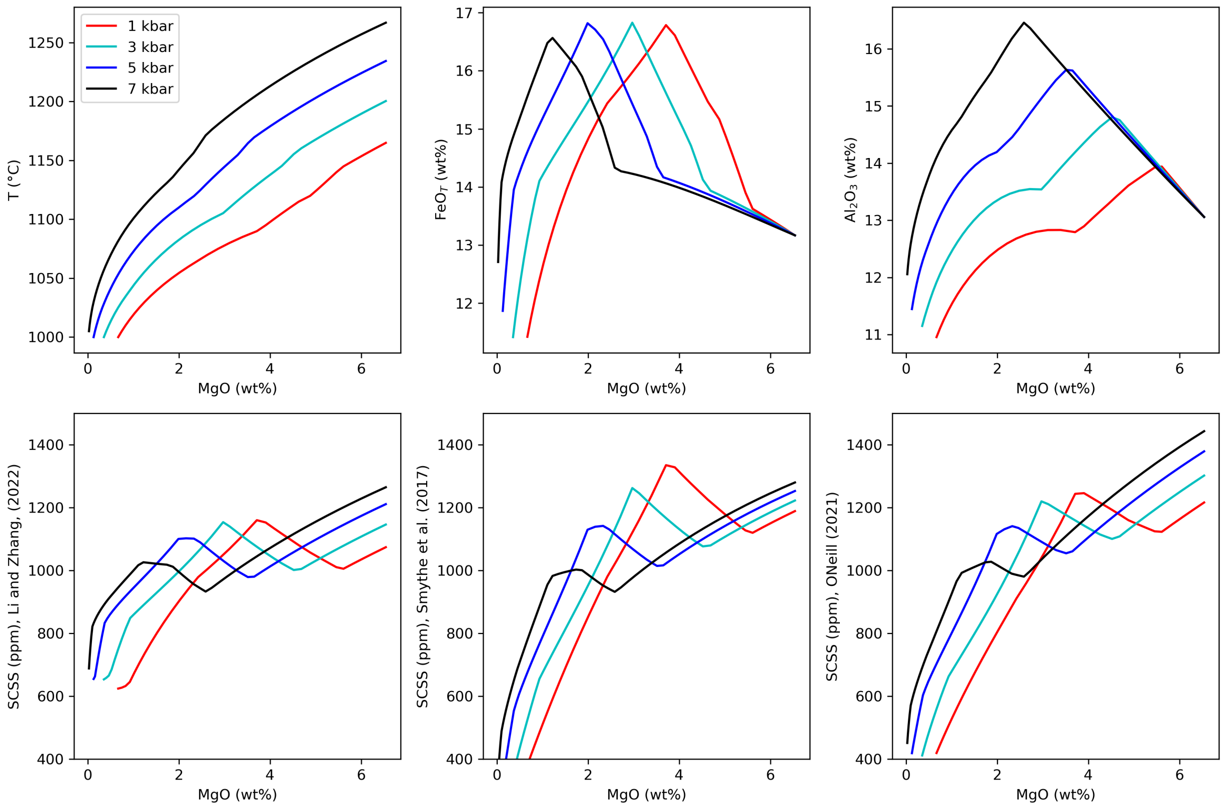


Figure 6: Integrating PyMELTScalc and PySulfSat to model SCSS for a fractional crystallization at 4 different pressures. Worked examples showing how to produce this and other similar plots are available on the ReadTheDocs page.

.

enough step size (i.e. small enough change in F), the results from these two approaches converge. However, using the limited number of columns supplied in the spreadsheet of Lee et al. [2012], the divergence can be several 10s of ppm at a given extent of melting (F).

We implement the non-modal melting version of Wieser et al. [2020] in PySulfSat as the function `Lee_Wieser_sulfide_melting`. This can be used to model the concentration of any element during near fractional batch melting. The user must simply supply a dataframe with partition coefficients for silicate and sulfide phases, and the mass proportion of each phase. This function allows the contrasting behavior of chalcophile and lithophile elements to be modeled (e.g., Ba vs. Cu, Wieser et al. [2020]). In Fig. 7a-b, we calculate the concentration of Cu and Ba in aggregated melts for different melt extents. First, we specify the silicate modes:

```
Modes=pd.DataFrame(data={'ol': 0.6, 'opx': 0.2,
      'cpx': 0.18, 'sp': 0.02, 'gt': 0}, index=[0])
```

And the partition coefficients:

```
KDs_Cu=pd.DataFrame(data={'element': 'Cu',
        'ol': 0.048, 'opx': 0.034,
        'cpx': 0.043, 'sp': 0.223,
        'gt': 0, 'sulf': 800}, index=[0])

KDs_Ba=pd.DataFrame(data={'element': 'Ba',
        'ol': 0.000005, 'opx': 0.000006,
        'cpx': 0.0004, 'sp': 0.223,
        'gt': 0.00007, 'sulf': 0 }, index=[0])
```

For simplicity in this example, we assume that the silicate modes stay fixed throughout the melting interval. This assumption makes very little difference for Cu, as the partition coefficient is substantially higher for sulfides than any silicate phases. Even for Ba, this is a reasonable 1st order assumption because it is extremely incompatible.

The other required inputs are the number of iterative steps (`N=3000`), the S content of the mantle source in ppm (`S_Mantle=[200]`), the concentration of S in mantle sulfides in ppm (`S_Sulf=360000`), the initial concentration of the element of interest in the mantle prior to melting in ppm (`elem_Per=30`), the S^{2-} concentration of the melt in ppm (`S_Melt_SCSS_2=1000`). There is also an option to specify the proportion of S^{6+} (`Prop_S6=0`, which will be used alongside the S^{2-} concentration to calculate the total amount of S in the melt using equation 6:

```
df_Cu_200S=ss.Lee_Wieser_sulfide_melting(N=3000,
Modes=Modes, KDs=KDs_Cu, S_Mantle=[200],
S_Sulf=360000, S_Melt_SCSS_2=1000,
elem_Per=30, Prop_S6=0)
```

Similarly for Ba:

```
df_Ba_200S=ss.Lee_Wieser_sulfide_melting(N=3000,
Modes=Modes, KDs=KDs_Ba, S_Mantle=[200],
S_Sulf=360000, S_Melt_SCSS_2=1000,
elem_Per=6.85, Prop_S6=0)
```

These calculations were run at `S_Mantle` contents of 100 ppm, 200 ppm and 300 ppm to produce Fig. 7a-b).

In addition to the ease of the above calculations vs. existing tools, the other substantial advantage of PySulfSat is that it provides access to melting models, models for partition coefficients in sulfides, and models of the SCSS within a single calculation environment. This enables a more sophisticated modeling approach than that of Lee et al. [2012] or Wieser et al. [2020]. Many existing modelling studies have assumed a fixed S content in the melt. However, in reality, the major element composition of instantaneous melts will change as melting proceeds (particularly for incompatible elements such as Na_2O and K_2O). Consequently, the SCSS will change during melting, rather than being set at a fixed value. The cyan line in Fig. 7c-e shows calculations using instantaneous melt compositions estimated from a Thermocalc melting model (Jennings and Holland [2015]). These melt compositions were used to calculate the SCSS, and modal abundances of silicate minerals from this model were also input. This model using a calculated SCSS has a higher S content in the initial melts than the model assuming S=1000 ppm throughout, resulting in a lower sulfide mode, a lower bulk K_D, and thus a higher Cu concentration in mantle melts at low F values (cyan vs. dashed magenta line, Fig. 7). Sulfide is also exhausted at a lower F (black star, part c). Both cyan and magenta models assume K_D for sulfide-melt is fixed at 800. PySulfSat contains the model of Kiseeva and Wood [2015] allowing the K_D to be calculated as a function of temperature, liquid FeO content, and the Ni and Cu content of the sulfide. This results in a substantially lower K_D, and thus even higher Cu contents. Additional information on how to perform these more advanced models can be found on the ReadTheDocs page. Overall, PySulfSat gives substantially more flexibility to explore concentrations in instantaneous and aggregated melts for all elements during melting in the presence of sulfide phases.

8 OTHER USEFUL FUNCTIONS

We also include a number of functions for other common workflows associated with S. For example, the functions `convert_d34_to_3432S` and `convert_3432S_to_d34` can be used to convert between $\delta\ ^{34}S$ values and $^{34}S/^{32}S$ ratios. By default, these functions use the the Vienna-CDT value of 1/22.6436 from Ding et al. [2001], although this can

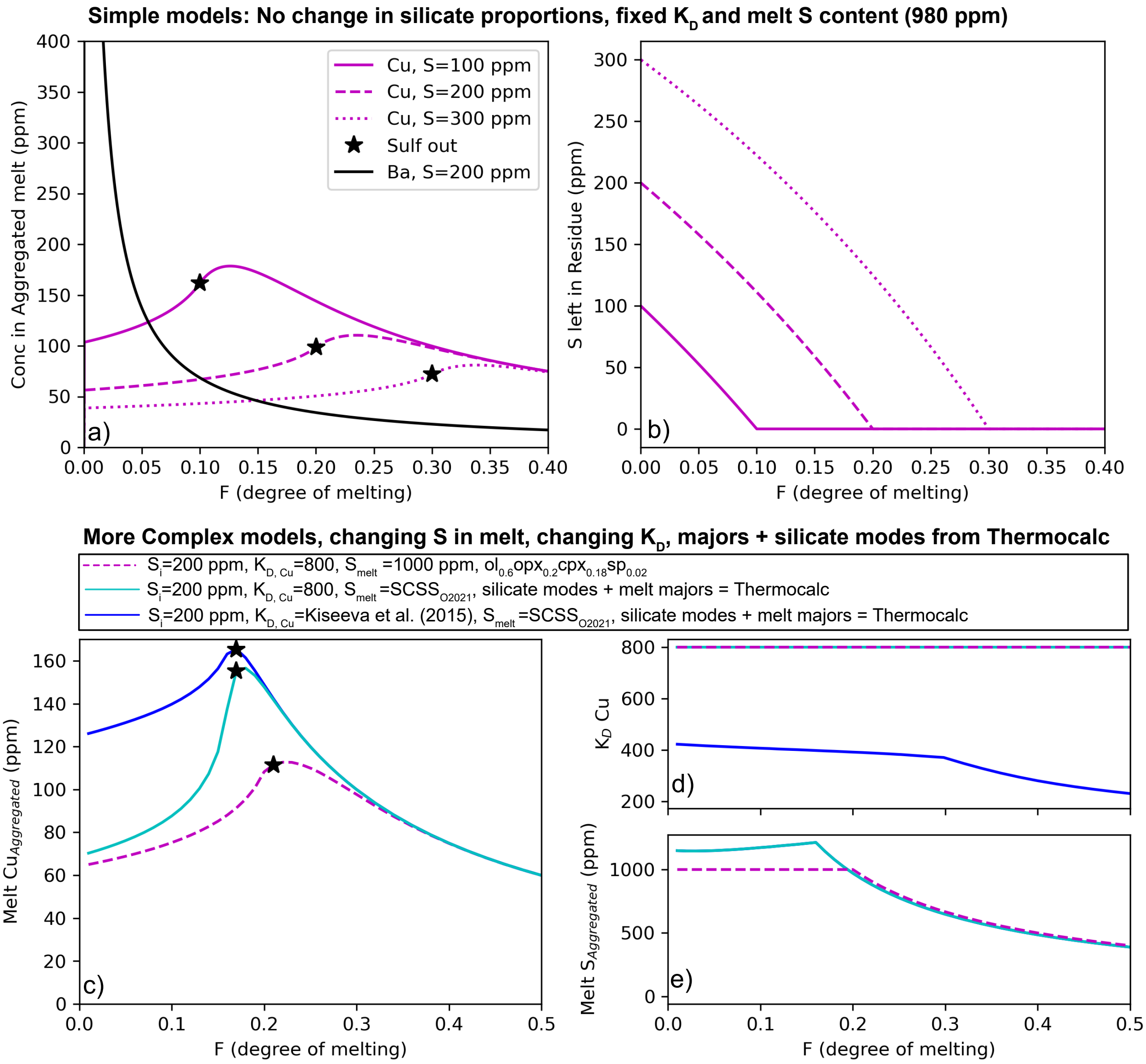


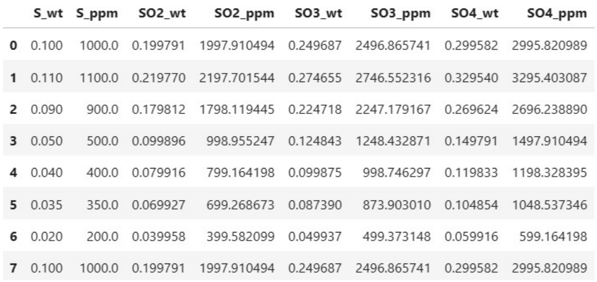
Figure 7: Modelling chalcophile elements during mantle melting. a-b) Simple models following Lee et al. [2012] and Wieser et al. [2020] where the K_D in the sulfide, the modal proportion of silicate minerals and S in the melt is kept constant throughout the melting interval. Variation in elemental concentrations correlate with the initial S content of the mantle source. c-e) More complex models combining melting models with K_D and SCSS functions within PySulfSat. For 200 ppm S in the mantle source, sustantially different trajectories can be generated by simply varying the model for the amount of S in the melt, or the partition coefficient of Cu. The cyan and blue lines use a mantle melting model from Thermocalc to obtain the major element contents and temperature of instantaneous melts. This allows the S content of these melts to be determined using the SCSS model of O'Neill [2021], assuming mantle sulfides contain 20 wt% Ni and 5 wt% Cu (after Ding and Dasgupta [2018]). The cyan line uses a fixed K_D for Cu (800, after Lee et al. [2012]). The blue line uses K_D calculated from the instantaneous silicate melt composition from Kiseeva and Wood [2015]. All models assume there is 30 ppm Cu in the mantle source.

be overwritten with any value of interest (using the input `st_ratio`). For example, if a dataframe is loaded in with a column for d34S the isotope ratio can be calculated as follows:

```
S3432=ss.convert_d34_to_3432S(d34S=df['d34S'])
```

We also include a function which allows users to enter S as S, SO_2, SO_3, or SO_4 in ppm or wt%, and calculates the concentration of all other S species:

```
df=ss.convert_S_types(S_ppm=df['S_ppm'])
```



	S_wt	S_ppm	SO2_wt	SO2_ppm	SO3_wt	SO3_ppm	SO4_wt	SO4_ppm
0	0.100	1000.0	0.199791	1997.910494	0.249687	2496.865741	0.299582	2995.820989
1	0.110	1100.0	0.219770	2197.701544	0.274655	2746.552316	0.329540	3295.403087
2	0.090	900.0	0.179812	1798.119445	0.224718	2247.179167	0.269624	2696.238890
3	0.050	500.0	0.099896	998.955247	0.124843	1248.432871	0.149791	1497.910494
4	0.040	400.0	0.079916	799.164198	0.099875	998.746297	0.119833	1198.328395
5	0.035	350.0	0.069927	699.268673	0.087390	873.903010	0.104854	1048.537346
6	0.020	200.0	0.039958	399.582099	0.049937	499.373148	0.059916	599.164198
7	0.100	1000.0	0.199791	1997.910494	0.249687	2496.865741	0.299582	2995.820989

Additionally, the studies of Kiseeva and Wood [2015] and Brenan [2015] parameterize K_Ds as a function of melt composition, and sulfide composition for Kiseeva and Wood [2015]. The function `calculate_sulfide_kds` can be used to calculate these partition coefficients.

9 FUTURE WORK AND CITATION

The open-source nature of PySulfSat, along with recent increase in interest in the behavior of S in magmas, means that this tool will continuously evolve. The current author team will endeavor to add new models as they are released, and anyone can submit new code using a pull request on GitHub (or by contacting the authors). Thus, users should check the ReadTheDocs page, where examples demonstrating new functionality beyond that described in this manuscript will be added in the future. New versions of PySulfSat can be obtained by running the following code in a Jupyter environment:

```
!pip install PySulfSat --upgrade
```

When citing calculations performed in PySulfSat in papers, users should be sure to specify which version they used, which can be obtained using:

```
ss.__version__
```

For example, the text may read "SCSS calculations were performed using the model of Smythe et al. [2017] implemented in PySulfSat v.1.0.3 (Wieser and Gleeson, 2023)." It is important to also cite all the original papers used to perform calculations (e.g. the SCSS model, the model for S^{6+}), as well as citing PySulfSat.

At present, there is no open-source code that can model sulfide and sulfate saturation with all the most recent models, and the behavior of S during degassing from a a silicate melt. We hope that in future, the PySulfSat source code can be integrated with the wide variety of S degassing tools becoming available to produce a single, coherent model engine for modeling S behavior in silicate melts.

10 CONCLUSIONS

PySulfSat is a open-source Python3 tool motivated by the FAIR research framework (Findable, Accessible, Interoperable, and Reusable). It will greatly speed up calculations, allow more inter comparison between models, and through its ease of implementation with Python, allow more detailed and robust investigations of the behavior of sulfur in magmatic systems.

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AUTHOR CONTRIBUTIONS

PW conceived the project, wrote the S-based code and the manuscript. MG build the fractional crystallization MELTS functions allowing integrating of PyMELTScalc with PySulfSat, and contributed to manuscript editing and code testing.

DATA AVAILABILITY

All files are available on GitHub (`https://github.com/PennyWieser/PySulfSat`). YouTube videos explaining various aspects of the tool are available on the PySulfSat YouTube channel `bit.ly/PySulfSatYouTube`, and Jupyter Notebook examples are available on the ReadTheDocs page (`bit.`

ly/PySulfSatRTD). The PyMELTScalc code is available on GitHub (https://github.com/gleesonm1/pyMELTScalc), and a follow up publication will describe this MELTS code in more detail.

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