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

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We are trying something innovative! We want you all to have a chance to play with the code, read the paper, and make suggestions of what can be improved/what models can be added BEFORE its even submitted!

So 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, a new Open-Source Python3 tool for modelling sulfide and sulfate saturation in magmas. Accurately predicting the onset of sulfide or sulfate saturation during fractional crystallization, and/or identifying melt compositions as saturated or undersaturated, is vital to understand and model the behavior of S-loving chalcophile elements during mantle melting, crustal storage and shallow degassing. PySulfSat can calculate the sulfide content at sulfide content at sulfide saturation ($SCSS^{2-}$) and the sulfate content at anhydrite saturation ($SCAS^{6+}$) using a number of the most recent models. It is extremely fast, performing calculations for each composition in ~1 ms on a standard laptop (16 GB RAM) meaning it can be applied to very large datasets with ease. PySulfSat also supports a variety of different input structures (spreadsheets, Petrolog3 outputs, MELTS tbl files, etc.), without requiring extensive formatting by the user. It can also be integrated with MELTS for python infrastructure, allowing calculations of sulfur solubility during fractional crystallization over a wide range of conditions within a single Jupyter Notebook. Importantly, PySulfSat allows mixing and matching methods, so the $SCSS^{2-}$ could be calculated with one model using the sulfide composition predicted by a different $SCSS^{2-}$ model. PySulfSat also contains functions for calculating the proportion of S^{6+} using popular expressions, along with other common workflows (e.g., calculating the mass proportion of fractionated sulfide). Worked examples are available on the Read The Docs page (https://bit.ly/PySulfSatRTD).

1 Introduction

Modelling solubility of sulfur in a silicate melt provides vital insights into the evolution of sulfur and other S-loving (chalcophile) elements during mantle melting (Ding and Dasgupta [2018]) and crustal processes such as fractional crystallization (Wieser et al. [2020]; Reekie et al. [2019]; Virtanen et al. [2022]; Muth and Wallace [2022]) and crustal assimilation (Virtanen et al. [2022]). Modeling the removal of sulfides and sulfate phases is particularly vital to understand the formation of economical deposits of chalcophile elements, the sulfur and metal flux emitted to the atmosphere during volcanic eruption, and the release of these environmentally reactive elements into 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 maximum amount of sulfide (S^{2-}) that can dissolve in a silicate melt before it becomes saturated in a sulfide phase, termed the sulfide content at sulfide saturation ($SCSS^{2-}$, e.g., Smythe et al. [2017]; O'Neill [2021]; Fortin et al. [2015]; Li and Ripley [2009]). There are also numerous models quantifying the amount of sulfate (S^{6+}) that can dissolve in a silicate melt before it becomes saturated in anhydrite, termed the sulfate content at anhydrite saturation (SCAS) (Chowdhury and Dasgupta [2019], Zajacz and Tsay [2019], Masotta and Keppler [2015], Baker and Moretti [2011], Li and Ripley [2009]), even though the sulfate phase may actually be a sulfate liquid at high temperatures (Jugo et al. [2005]). 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. Smythe et al. [2017] and Jugo et al. [2010] produce models characterizing the proportion of these two species, which can be used alongside $SCSS^{2-}$ and $SCAS^{6+}$ calculations to obtain the total amount of S that is dissolved in the melt. Kleinsasser et al. [2022] quantify the location of this transition specifically for dacitic melt compositions.

2 Previously-available tools

At the moment, $SCSS^{2-}$ and $SCAS^{6+}$ calculations are performed in spreadsheets supplied by the author (e.g., Smythe et al. [2017]; O'Neill [2021]; Fortin et al. [2015]), or in the case of no support-

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ing tool being provided, individuals must produce their own method to perform calculations. The available spreadsheets require users to paste in their melt compositions with oxides in a specific order (the order differs between spreadsheets). 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. To compare different models, the outputs must be re-extracted (difficult to do automatically given the formatting of each spreadsheet) and compiled in a single location for plotting.

An additional compilation arises from the fact that the three most recent $SCSS^{2-}$ models (Smythe et al. [2017], O'Neill [2021], Li and Zhang [2022]) account for the amount of Ni and Cu in the sulfide, which lowers the $SCSS^{2-}$ relative to calculations performed for pure Fe-S sulfides (e.g., Fortin et al. [2015]). However, the ways to input and calculate the sulfide composition in these spreadsheets differs, making it hard to directly compare outputs from these models. The Smythe et al. [2017] Excel workbook has two sheets, one in which users can enter the sulfide composition in wt%, and another where the sulfide composition is solved using partition coefficients from Kiseeva and Wood [2015] and an estimate of the Ni and Cu content in the melt. In contrast, by default 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), or the user can overwrite this with a fixed value of Fe/(Fe+Cu+Ni). The spreadsheet of Li and Zhang [2022] relies on users inputting 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.

3 PySulfSat: An Open-source approach

To address the tedium associated with performing $SCSS^{2-}$ and $SCAS^{6+}$ calculations in existing spreasheets, and difficulties associated with comparing models, we produce 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, 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
```

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

Example Jupyter Notebooks showing worked examples for calculating $SCSS^{2-}$ and $SCAS^{6+}$ for different melt compositions from a variety of input structures (e.g. an excel spreadsheet of compositions measured by XRF or microprobe, and outputs from Petrolog3 and MELTS, Danyushevsky and Plechov [2011]; Ghiorso and Sack [1995]; Gualda et al. [2012]) can be found on the Read The Docs page (bit.ly/PySulfSatRTD). We anticipate that users new to python will simply download and then adapt these notebooks to read in their data files of interest.

4 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

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 load in 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 `Si02_melt` from Petrolog3 into `Si02_Liq`).

Geological Abbreviations

SCSS	Sulfide content at sulfide saturation
SCAS	Sulfate content at sulfate 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 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)
pandas Series	A 1D column of data
NumPy (np.)	A Python library that handles the math used in PySulfSat (e.g., log, exp)
Matplotlib (plt.)	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

5 Available functions

PySulfSat implements the most recent SCSS^{2-} and SCAS^{6+} models (Fig. 2), as well as containing functions to help with other common workflows (showcased in more detail on the Read The Docs page). The open-source nature of PySulfSat means we anticipate more functionality will be added in future (e.g. incorporating new SCSS^{2-} and SCAS^{6+} models, and new workflows using these models).

6 SCSS^{2-} models

Numerous examples of how to model sulfide saturation can be found on the Read The Docs page. In Figure 3, the SCSS^{2-} is calculated for a sulfide composition measured using Energy Dispersive Spectroscopy (EDS, Fe/(Fe+Ni+Cu)=0.65, e.g., Wieser et al. [2020]) using the SCSS^{2-} models of Smythe et al. [2017], O'Neill [2021], and Li and Zhang [2022]. The expected increase in S content with fractional crystallization without the formation of a S-bearing phase is also calculated for comparison (black dashes), and these different S trajectories are plotted using matplotlib.

6.1 Calculating Sulfide Compositions

Using a measured sulfide composition is the simplest, and most reliable method to perform SCSS^{2-} calculations with the most recent generation of SCSS^{2-} models that require a sulfide composition. However, in many systems, direct measurements of sulfide compositions do not exist. 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 Fe/(Fe+Ni+Cu) ratio using an empirical expression:

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

Where :

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

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 Measured Ni and Cu content in the melt and the predicted value:

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

Using the Excel solver function, the contents of Cu and Ni in the sulfide are varied to minimise this residual. Using the equation of Kiseeva and Wood [2015] to calculate the Fe content of the sulfide, along with the best matching Ni and Cu sulfide content, the Fe/(Fe+Ni+Cu) in the sulfide can be calculated. 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 use these calculated sulfide compositions, instead of specifying a constant for the `Fe_FeNiCu_Sulf` argument as in Fig. 3, users can enter the strings `'Calc_Smythe'` or `'Calc_ONeill'` into any of the SCSS^{2-} models which require a sulfide composition (Fig. 2). For example, to use the Smythe et al. [2017] SCSS^{2-} model with the O'Neill [2021] calculated sulfide composition:

```
S17_SCSS_S17_Sulf=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="Calc_ONeill",
Ni_Liq=Liqs['Ni_Liq (ppm)'],
Cu_Liq=Liqs['Cu_Liq (ppm)'])
```

Where `Ni_Liq (ppm)` and `Cu_Liq (ppm)` are columns in the inputted file containing estimated Ni and Cu contents of the melt in ppm.

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

```
O21_SCSS_S17_Sulf=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="Calc_Smythe",
Ni_Liq=Liqs['Ni_Liq (ppm)'],
Cu_Liq=Liqs['Cu_Liq (ppm)'])
```

Reference	Name in PySulfSat	T-sens?	P-sens?	H_2O-sens?	*Redox sensitive?*	Sulfide \Sulfate comp?
SCAS models						
Chowdhury & Dasgupta (2019)	"calculate_CD2019_SCAS"	✓	✗	✓	✗	✗
Zajacz & Tsay (2019)	"calculate_ZT2022_SCAS"	✓	✗	✓	✗	✗
SCSS models						
Li and Zhang (2022)	"calculate_LZ2022_SCSS"	✓	✓	✓	✓	✓
O'Neill (2021)	"calculate_O2021_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) adaptation of Kiseeva et al. (2015) method	"Calc_Smythe"	✓	✗	✗	✓	

Calculating Proportion of S^{6+}

Reference	Name in PySulfSat	Parameters
Jugo et al. (2010)	"calculate_S6St_Jugo2010_eq10"	ΔQFM
Nash et al. (2019)	"calculate_S6St_Nash2019"	Fe^{3+}/Fe_T

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

Name in PySulfSat	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 a model for S^{6+}/S_T. 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/sulfate removed for a fractional crystallization path where the SCSS or SCAS is modelled

Figure 2: Supported Models in PySulfSat. $SCAS^{6+}$ models from Chowdhury and Dasgupta [2019] and Zajacz and Tsay [2019], $SCSS^{2-}$ models from Li and Zhang [2022], Liu et al. [2021], O'Neill [2021], Smythe et al. [2017] and Fortin et al. [2015]. S^{6+} corrections from Jugo et al. [2010] and Nash et al. [2019]. A function for calculating Total S from the $SCSS^{2-}$ and $SCAS^{6+}$ is also included (see section 8.

.

Load data from a Petrolog3 output file

	A	B	C	D	E	F	G	H	I	J	AY	AZ	BA
1	SiO2_mag	TiO2_mag	Al2O3_ma	Fe2O3_ma	FeO_mag	MnO_ma	MgO_ma	CaO_mag	Na2O_ma	K2O_mag	density	Ln(viscosit	Melt_%_m
2	49.901	0.9981	14.9715	0.9839	8.0964	0.0998	9.9763	11.9772	2.4953	0.1996	2.683	6.25	99.99
3	49.9978	1.0081	15.122	0.9743	8.0754	0.1008	9.6064	12.0976	2.5203	0.2016	2.682	6.38	98.995
4	50.0982	1.0185	15.277	0.9649	8.0492	0.1018	9.2279	12.2216	2.5462	0.2037	2.681	6.52	97.9904
5	50.2003	1.0289	15.4337	0.9561	8.0178	0.1029	8.8486	12.3469	2.5723	0.2058	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	Ni_Liq_p
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	6
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	6
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	5

Option 1: Calculate Smythe et al. (2017) SCSS (measured sulfide composition)

```
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 Petrolog

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	Si_XA_ideal	Ti_XA_ideal	Al_XA_ideal	Mg_XA_ideal
0	1163.723704	317.894143	-12643.824134	-77.425187	-2992.932034	-1910.028590
1	1132.276539	309.303728	-12681.503374	-78.282101	-3026.156769	-1841.118249
2	1099.610160	300.380260	-12720.419296	-79.173410	-3060.410799	-1770.448728

Scroll bar

Option 2: Calculate ONeill (2021) SCSS (measured sulfide composition)

```
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	CaO
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	11.
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	12.
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	12.

Option 3: Calculate Li & Zhang (2022) SCSS (measured sulfide composition)

```
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 S behaved entirely incompatibly (no sulfide formation)

```
FC=ss.crystallize_S_incomp(S_init=1000, F_melt=df_out['Melt_%_magma']/100)
```

Plot modelled SCSS vs. FC trajectory

```
fig, (ax1) = plt.subplots(1, 1, figsize=(4,3.5))
ax1.plot(df_out['MgO_Liq'], FC, ':k', label='Fractional Crystallization')
ax1.plot(Smythe_FixedSulf['MgO_Liq'],
Smythe_FixedSulf['SCSS_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.set_ylabel('S (ppm)')
ax1.set_xlabel('MgO Liq (wt%)')
ax1.legend(fontsize=8)
plt.xlim([4, 10])
plt.ylim([200, 1300])
fig.savefig('SCSS_Models.png', dpi=200, bbox_inches='tight')
```

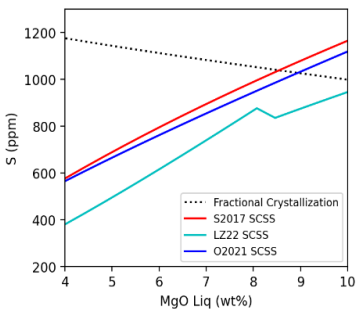

Figure 3: Example workflow showing how to calculate $SCSS^{2-}$ using different models from a Petrolog3 fractional crystallization model. If users want the non ideal $SCSS^{2-}$ from Smythe et al. [2017] as well as the ideal SCSS, they must also enter a value for `Ni_FeNiCu` and `Cu_FeNiCu` from their measured sulfide composition).

6.2 H_2O-sensitivity

Unlike the $SCSS^{2-}$ models of O'Neill [2021] and Smythe et al. [2017], the $SCSS^{2-}$ models of Fortin et al. [2015] 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).

For models which are sensitive to the ratio of Fe^{3+} in the liquid (Fig. 2), the user should specify an argument `Fe3Fet_Liq`, which could refer to any column name in the loaded data. Alternatively, users can specify a single value in the function, as for `H2O_Liq`, e.g., `Fe3Fet_Liq=0.15`. Finally, users can also the python package Thermobar Wieser et al. [2022] to convert a log fO_2 value or buffer position into a `Fe3Fet_Liq` ratio.

6.3 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 fractional 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 modelled solubility of Sulfur 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. 3:

```
S_Frac=ss.calculate_mass_frac_sulf(
S_model=ONeill_FixedSulf['SCSS2_ppm'],
S_sulf=320000, S_init=1600,
F_melt=df_out['Melt_\%_magma']/100)
```

7 $SCAS^{6+}$ models

$SCAS^{6+}$ models are calculated in a very similar way to $SCSS^{2-}$ models, with the simplification that anhydrite saturation models aren't currently parameterized with terms for the composition of the S-bearing phase, pressure, or Fe^{3+}/Fe_T (Fig. 2).

For example, using the data input from a Petrolog3 model as `df_out` (see Fig. 3), the $SCAS^{6+}$ using the model of Chowdhury and Dasgupta [2019] would be calculated as follows:

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

And 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, this returns the calculated $SCAS^{6+}$, all intermediate calculations, and the originally-loaded compositions.

8 Magmas with a mix of S^{2-} and S^{6+}

Silicate melts undergo a relatively abrupt transition 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. 4b). In systems where S is present with more than one redox state, the calculated $SCSS^{2-}$ (which quantifies the solubiliy of just S^{2-} species) and $SCAS^{6+}$ (which quantifies just the solubility of just S^{6+}) do not represent the total concentration of the S dissolved in the magma (Jugo [2009]).

To demonstrate the importance of considering the presence of S^{2-} and S^{6+} when modelling S solubility, we consider a melt with a $SCSS^{2-}$ of 1000 ppm, and a $SCAS^{6+}$ of 5000 ppm for ΔQFM bewteen -1 and 3. Equation 10 of Jugo et al. [2010] can be used to calculate the proportion of S^{6+}/S_T as a function of ΔQFM:

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

This equation can be implemented in PySulfSat as follows:

```
S6St_Q03=ss.calculate_S6St_Jugo2010_eq10(deltaQFM=0.3)
```

To produce Fig. 4, we produce a linearly-spaced numpy array of 10,001 points between ΔQFM=-1 and ΔQFM=3 using the `np.linspace` function, and calculate S^{6+}/S_T for every value along this array (cyan line, Fig. 4b).

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

At ΔQFM=-1 (point 1 on Fig. 4b), 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. 4a). 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]:

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

In PySulfSat this is implemented as follows:

```
SCSS_Tot=ss.calculate_SCSS_Total(SCSS=1000,
S6St_Liq=S6St)
```

The $SCSS_T$ is 1794, with 1000 ppm of S^{2-}, and 794 ppm of S^{6+} (see red and grey lines on Fig. 4b).

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. 4a). For example, at point 4 (ΔQFM=2), S^{6+}/S_T=0.988. Equation would predict that $SCSS_T$ is 80,432 ppm, with 1000 ppm of S^{2-}, and 79,432 ppm of S^{6+}, while the $SCAS^{6+}$ is only 5000 ppm.

To determine the total amount of sulfur dissolved in more oxidised melts, the $SCAS^{6+}$ must be corrected for the presence of S^{2-}:

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

In PySulfSat this is implemented as follows:

```
SCAS_Tot=ss.calculate_SCAS_Total(SCAS=5000,
S2St_Liq=1-S6St)
```

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.

The total amount of dissolved S in ΔQFM space is defined by the section of the $SCSS_T$ curve where S^{6+} does not exceed the $SCAS^{6+}$ (magenta solid line, Fig. 4a), and the section of the $SCAS_T$ curve where S^{2-} doesn't exceed the $SCSS^{2-}$ (black solid line, Fig. 4a). The combined curve meeting these requirements is shown as a green line in Fig. 4b.

It can also be helpful to think in terms of mass balance. At Point 3, S^{6+} is fixed at the $SCAS^{6+}$. We can write a mass balance for the amount of S^{2-} that can be present for the specified S^{6+}/S_T ratio and the amount of S^{6+} fixed by the $SCAS^{6+}$:

$$\frac{S^{6+}}{S_T} = \frac{SCAS^{6+}}{S^{2-} + SCAS^{6+}} \quad (8)$$

Which re-arranges to:

$$\begin{aligned} S^{2-} &= \frac{SCAS^{6+} - \frac{S^{6+}}{S_T} \times SCAS^{6+}}{\frac{S^{6+}}{S_T}} \\ &= (5000 - 0.833 \times 5000)/(0.833) \\ &= 1000\,ppm \end{aligned} \quad (9)$$

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 $SCAS^{6+}$.

At Point 4,

$$\begin{aligned} S^{2-} &= \frac{SCAS^{6+} - \frac{S^{6+}}{S_T} \times SCAS^{6+}}{\frac{S^{6+}}{S_T}} \\ &= (5000 - 0.988 \times 5000)/(0.988) \\ &= 62\,ppm \end{aligned} \quad (10)$$

So the total amount of dissolved S is 5000 + 62 (5062 ppm).

In PySulfSat, for any combination of $SCSS^{2-}$ and $SCAS^{6+}$ values, the total amount of S can be calculated using the function `calculate_S_Total_SCSS_SCAS`. Values from any $SCSS^{2-}$ and $SCAS^{6+}$ model in PySulfSat can be input, there are a variety of options to calculate S^{6+}/S_T.

For example, using 11 ΔQFM values between -1 and 3, calculations like those shown in Fig. 4 can be performed using the model of Jugo et al. [2010], for a fixed $SCSS^{2-}$ and $SCAS^{6+}$ value:

```
deltaQFM_lin=np.linspace(-1, 3, 11)
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. This

parameterizes S^{6+}/S_T in terms of the ratio of Fe^{3+} to Fe^{2+} and temperature (in Kelvin):

$$log(\frac{S^{6+}}{S^{2-}}) = 8log(\frac{Fe^{3+}}{Fe^{2+}}) + \frac{8.7436 \times 10^6}{T^2} - \frac{27703}{T} + 20.273 \quad (11)$$

This can be implemented as follows:

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

Alternatively, the user can simply specify `model='Nash'` 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 (ΔQFM=+1.81 $\pm$0.56). They provide two expressions for correcting the $SCSS^{2-}$ and $SCAS^{6+}$:

$$SCSS_T^{dacitic} = SCSS^{2-} * (1 - 10^{2\Delta QFM - 3.05})$$
$$SCAS_T^{dacitic} = SCAS^{6+} * (1 - e^{1.26 - 2\Delta QFM}) \quad (12)$$

To use this parameterization in the `calculate_S_Total_SCSS_SCAS` function, specify `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')
```

As well as using `calculate_S_Total_SCSS_SCAS` to calculate changes in the proportion of different species with ΔQFM to produce figures like Fig. 4, this function can also be used to calculate the maximum S solubility for any given sample (or set of samples) where the $SCSS^{2-}$ and $SCAS^{6+}$ have been calculated using any of the models in PySulfSat.

While it is tempting to use the simper expressions for correcting the SCSS or SCAS, it is safer to use this mixed function, as it ensures you have not corrected beyond the solubility of the other volatile species. In many tectonic settings, corrections for the total amount of S must be applied. XANES measurements on the majority of ocean-island basalts, as well as relatively mafic arc magmas, show non-negligible proportions of S^{6+} (Lerner et al. [2021], Brounce et al. [2017], Muth and Wallace [2021]). Unfortunately, different models for predicting S^{6+}/S_T can yield very different results, and do not always match direct XANES measurements (Wieser et al. [2020]; Lerner et al. [2021]). Thus, in an ideal world, when correcting the SCSS and SCAS, S^{6+}/S_T would be directly measured in the samples of interest. In this instance, instead of specifying a model, users should enter this as the argument `S6St_Liq` into the `calculate_S_Total_SCSS_SCAS` function (and then do not need to specify a model, `deltaQFM` or `Fe3Fet_Liq`).

Some users may have estimates of Fe^{3+}/Fe_T from techniques such as XANES, but did not measure S^{6+}/S_T, so want to use the model of Jugo et al. [2010]. The python package Thermobar (Wieser et al. [2022]) can be used to convert between fO_2 values, buffer positions and `Fe3FeT_Liq` ratios. For example, the Petrolog3 output in figure 3 has a column for the log of the fO_2 value:

```
!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:

```
Calc_Jugo_S6=ss.calculate_S6St_Jugo2010(
DeltaQFM=Buffer_calc['deltaQFM_Frost1991'])
```

9 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 (using Thermoengine, Johnson et al. [2022], or MELTS for Python, see Antoshechkina and Ghiorso [2018]). Here, we make use of the PyMELTScalc python package (see https://github.com/gleesonm1/pyMELTScalc), which has inbuilt functions for fractional crystallization, and returns output structures consistent with the required inputs for PySulfSat.

After installing PyMELTScalc (see example on Read The Docs), this package should be importing it into the notebook:

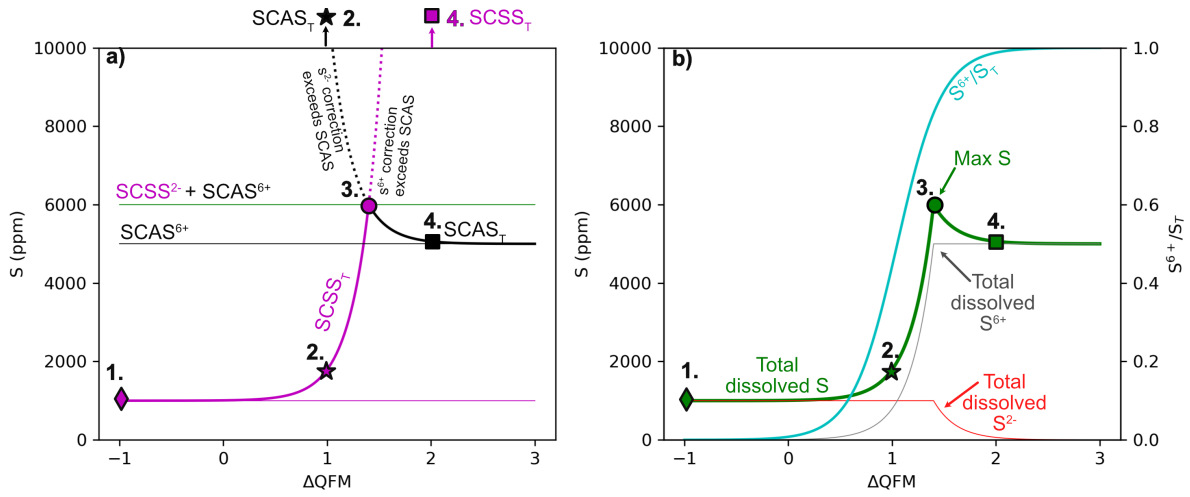

Figure 4: Calculating the total amount of dissolved S by applying corrections to the $SCSS^{2-}$ and $SCAS^{6+}$ using the model of Jugo et al. [2010] in the function `calculate_S_Total_SCSS_SCAS`.

```
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_out2.iloc[0]
```

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

```
MELTS_FC=M.multi_iso_crystallize(
model="MELTSv1.0.2",
comp = sample.to_dict(),
P_path_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_path_bar`), starting at the wet liquidus (as `find_liquidus=True`), and runs until 700C (`T_end_C`, unless the MELTS calculation doesnt converge after 100 quadratic minimisation attempts, in which case it may end at a higher temperature. The temperature step is 5 C (`dt_C`), the `Fe3Fet_Liq` ratio is set at 0.1, and both fluids and solids are fractionated.

The `multi_iso_crystallize` 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. `Si02_Liq`, `Si02_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. 5 shows the $SCSS^{2-}$ calculated for fractional crystallization models run at 4 different pressures from a single call to the PyMELTScalc `multi_iso_crystallize` function.

10 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

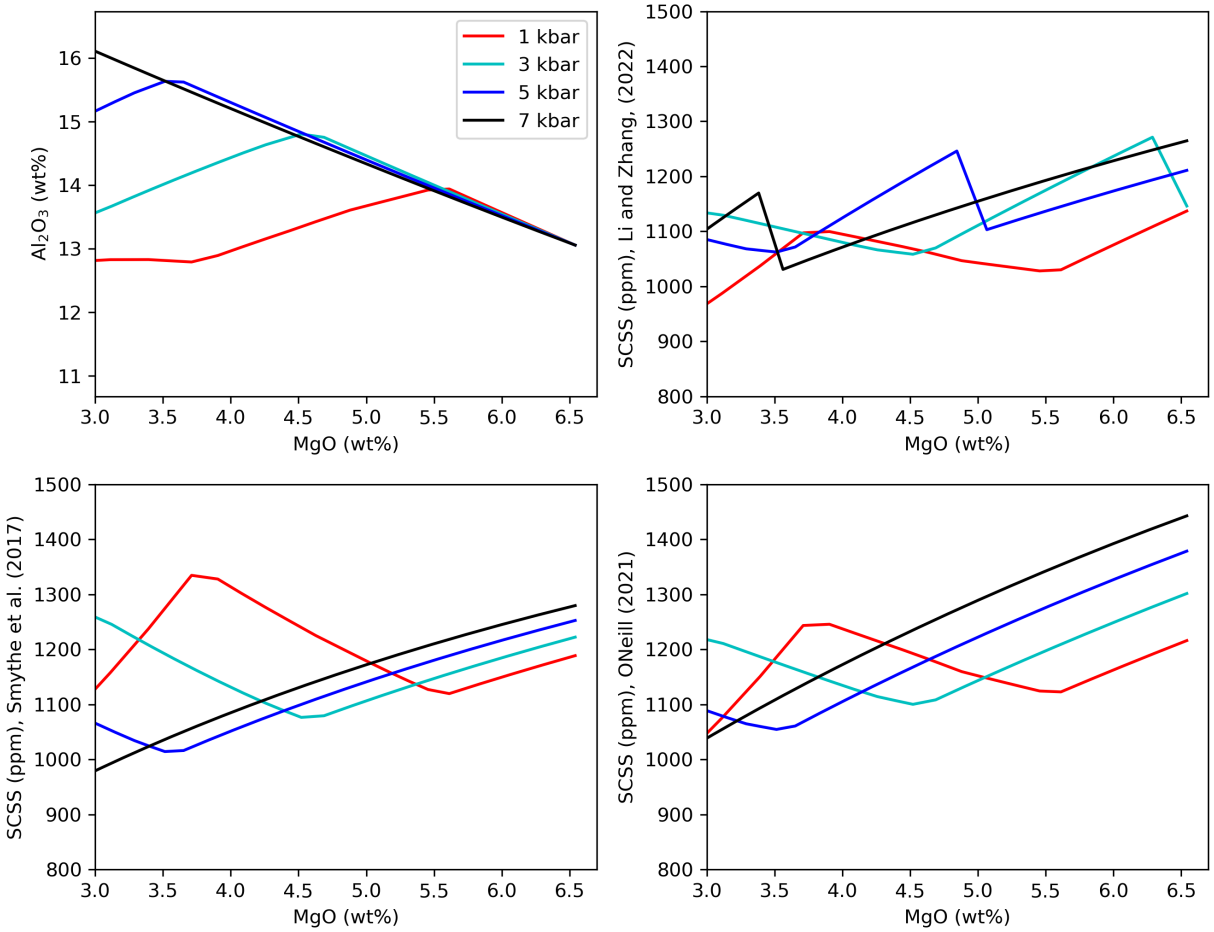

Figure 5: Example PyMELTScalc run at 4 pressures, with $SCSS^{2-}$ calculated using three different models in PySulfSat. Worked example showing how to produce this plot available on the Read The Docs page.
.

models as they are released, and anyone can submit new code using a pull request on GitHub (or by contacting the authors). Thus, interested users should check the Read The Docs 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)."

11 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, and wrote the S-based code. MG build the fractional crystallization MELTS functions allowing integrating of PyMELTScalc with PySulfSat.

Data availability

All files are avaiable 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 Read The Docs 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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