S7_Testing_Shishkina_et_al_2014

March 30, 2021

1 This notebook compares the outputs from VESIcal to the Shishkina et al. (2014) Calibration dataset.

- This notebook relies on the Excel spreadsheet entitled: "S7_Testing_Shishkina_et_al_2014.xlsx"
- Test 1 compares the experimental pressures in the calibration dataset of Shishkina et al. (2014) for H_2O-only experiments to the saturation pressures obtained from VESIcal for the "ShishkinaWater" model.
- Test 2 compares the experimental pressures in the calibration dataset of Shishkina et al. (2014) for CO_2-only experiments to the saturation pressures obtained from VESIcal for the "ShishkinaCarbon" model.
- Test 3 compares the experimental pressures for mixed H_2O-CO_2 bearing fluids presented in Table 2 of the main text to the saturation pressures obtained from VESIcal for the "Shishkina" model.
- Test 4 justifies the approach used in VESIcal, where cation fractions for their equation 9 are calculated ignoring H_2O and CO_2

[1]:
```
import VESIcal as v
import matplotlib.pyplot as plt
import numpy as np
from IPython.display import display, HTML
import pandas as pd
import matplotlib as mpl
import seaborn as sns
from sklearn.linear_model import LinearRegression
from sklearn.metrics import r2_score
import statsmodels.api as sm
from statsmodels.sandbox.regression.predstd import wls_prediction_std
%matplotlib inline
```

[2]:
```
sns.set(style="ticks", context="poster",rc={"grid.linewidth": 1,"xtick.major.
↪width": 1,"ytick.major.width": 1, 'patch.edgecolor': 'black'})
plt.style.use("seaborn-colorblind")
plt.rcParams["font.size"] =12
plt.rcParams["mathtext.default"] = "regular"
plt.rcParams["mathtext.fontset"] = "dejavusans"
plt.rcParams['patch.linewidth'] = 1
```

```
plt.rcParams['axes.linewidth'] = 1
plt.rcParams["xtick.direction"] = "in"
plt.rcParams["ytick.direction"] = "in"
plt.rcParams["ytick.direction"] = "in"
plt.rcParams["xtick.major.size"] = 6 # Sets length of ticks
plt.rcParams["ytick.major.size"] = 4 # Sets length of ticks
plt.rcParams["ytick.labelsize"] = 12 # Sets size of numbers on tick marks
plt.rcParams["xtick.labelsize"] = 12 # Sets size of numbers on tick marks
plt.rcParams["axes.titlesize"] = 14 # Overall title
plt.rcParams["axes.labelsize"] = 14 # Axes labels
plt.rcParams["legend.fontsize"]= 14
```

1.1 Test 1 and 2 - comparing saturation pressures to experimental pressures

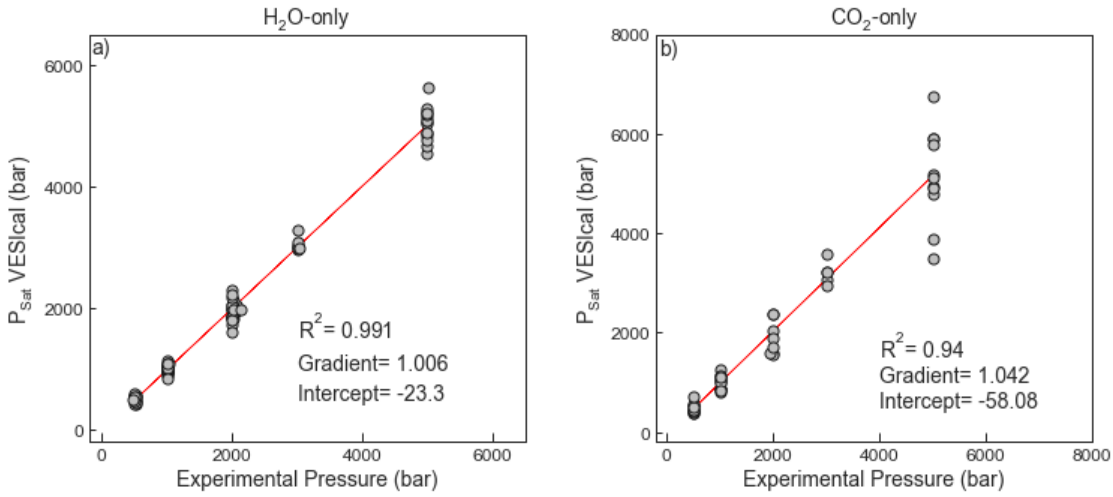
[3]:
```
myfile_CO2 = v.BatchFile('S7_Testing_Shishkina_et_al_2014.xlsx',␣
 ↪sheet_name='CO2') # Loading Carbon calibration dataset
satPs_wtemps_Shish_CO2= myfile_CO2.
 ↪calculate_saturation_pressure(temperature="Temp", model='ShishkinaCarbon') #␣
 ↪Calculating saturation pressures
myfile_H2O = v.BatchFile('S7_Testing_Shishkina_et_al_2014.xlsx',␣
 ↪sheet_name='H2O') # Loading Water calibration dataset
satPs_wtemps_Shish_H2O= myfile_H2O.
 ↪calculate_saturation_pressure(temperature="Temp", model='ShishkinaWater') #␣
 ↪Calculating Saturation pressures
```

```
/Users/kiacovin/Dropbox/Research/__Manuscripts in Progress/__VESIcal/__TheCode/V
ESIcal/manuscript/Supplement/JupyterNotebooks/Shishkina/VESIcal/calculate_classe
s.py:301: RuntimeWarning: Saturation pressure not found.
  satP = self.model.calculate_saturation_pressure(sample=sample,**kwargs)
```

[4]:
```
######################## H2O only experiments
# This calculating a linear regression, and plots experimental pressures vs.␣
 ↪saturation pressures for the Water calibration dataset
X_Test1=satPs_wtemps_Shish_H2O['Press']
Y_Test1=satPs_wtemps_Shish_H2O['SaturationP_bars_VESIcal']
mask_Test1 = (X_Test1>-1) & (Y_Test1>-1) # This gets rid of Nans
X_Test1noNan=X_Test1[mask_Test1].values.reshape(-1, 1)
Y_Test1noNan=Y_Test1[mask_Test1].values.reshape(-1, 1)
lr=LinearRegression()
lr.fit(X_Test1noNan,Y_Test1noNan)
Y_pred_Test1=lr.predict(X_Test1noNan)

fig, (ax1, ax2) = plt.subplots(1,2, figsize=(12,5)) # adjust dimensions of␣
 ↪figure here
```

```
ax1.plot(X_Test1noNan,Y_pred_Test1, color='red', linewidth=0.5, zorder=1) #␣
 ↪This plots the best fit line
ax1.scatter(satPs_wtemps_Shish_H2O['Press'],␣
 ↪satPs_wtemps_Shish_H2O['SaturationP_bars_VESIcal'],  s=50, edgecolors='k',␣
 ↪facecolors='silver', marker='o', zorder=5)
# This bit plots the regression parameters on the graph
I='Intercept= ' + str(np.round(lr.intercept_, 1))[1:-1]
G='Gradient= '  + str(np.round(lr.coef_, 3))[2:-2]
R='R$^2$= ' +  str(np.round(r2_score(Y_Test1noNan, Y_pred_Test1), 3))

ax1.text(3000, 1500, R, fontsize=14)
ax1.text(3000, 1000, G, fontsize=14)
ax1.text(3000, 500, I,  fontsize=14)

###################  CO2 experiments

X_Test2=satPs_wtemps_Shish_CO2['Press']
Y_Test2=satPs_wtemps_Shish_CO2['SaturationP_bars_VESIcal']
mask_Test2 = (X_Test2>-1) & (Y_Test2>-1) # This gets rid of Nans
X_Test2noNan=X_Test2[mask_Test2].values.reshape(-1, 1)
Y_Test2noNan=Y_Test2[mask_Test2].values.reshape(-1, 1)
lr=LinearRegression()
lr.fit(X_Test2noNan,Y_Test2noNan)
Y_pred_Test2=lr.predict(X_Test2noNan)
ax2.plot(X_Test2noNan,Y_pred_Test2, color='red', linewidth=0.5, zorder=1) #␣
 ↪This plots the best fit line
ax2.scatter(satPs_wtemps_Shish_CO2['Press'],␣
 ↪satPs_wtemps_Shish_CO2['SaturationP_bars_VESIcal'],  s=50, edgecolors='k',␣
 ↪facecolors='silver', marker='o', zorder=5)
# This bit plots the regression parameters on the graph
I='Intercept= ' + str(np.round(lr.intercept_, 2))[1:-1]
G='Gradient= '  + str(np.round(lr.coef_, 3))[2:-2]
R='R$^2$= ' +  str(np.round(r2_score(Y_Test2noNan, Y_pred_Test2), 2))

ax2.text(4000, 500, I, fontsize=14)
ax2.text(4000, 1000, G, fontsize=14)
ax2.text(4000, 1500, R, fontsize=14)

ax1.set_xlabel('Experimental Pressure (bar)', fontsize=14)
ax1.set_ylabel('P$_{Sat}$ VESIcal (bar)', fontsize=14)
ax2.set_xlabel('Experimental Pressure (bar)', fontsize=14)
ax2.set_ylabel('P$_{Sat}$ VESIcal (bar)', fontsize=14)
ax1.set_xticks([0, 2000, 4000, 6000, 8000, 10000])
ax1.set_yticks([0, 2000, 4000, 6000, 8000, 10000])
ax2.set_xticks([0, 2000, 4000, 6000, 8000, 10000])
ax2.set_yticks([0, 2000, 4000, 6000, 8000, 10000])
ax1.set_xlim([-200, 6500])
```

```
ax1.set_ylim([-200, 6500])
ax2.set_xlim([-200, 8000])
ax2.set_ylim([-200, 8000])
plt.subplots_adjust(left=0.125, bottom=None, right=0.9, top=None, wspace=0.3,␣
↪hspace=None)

ax1.text(-150, 6200, 'a)', fontsize=14)
ax2.text(-150, 7600, 'b)', fontsize=14)
ax1.set_title('H$_{2}$O-only',  fontsize=14)
ax2.set_title('CO$_2$-only',  fontsize=14)
fig.savefig('Shishkina_Test1and2.png', transparent=True)
```



1.2 Test 3 - Mixed H_2O - CO_2 experiments from Table 2 in the text.

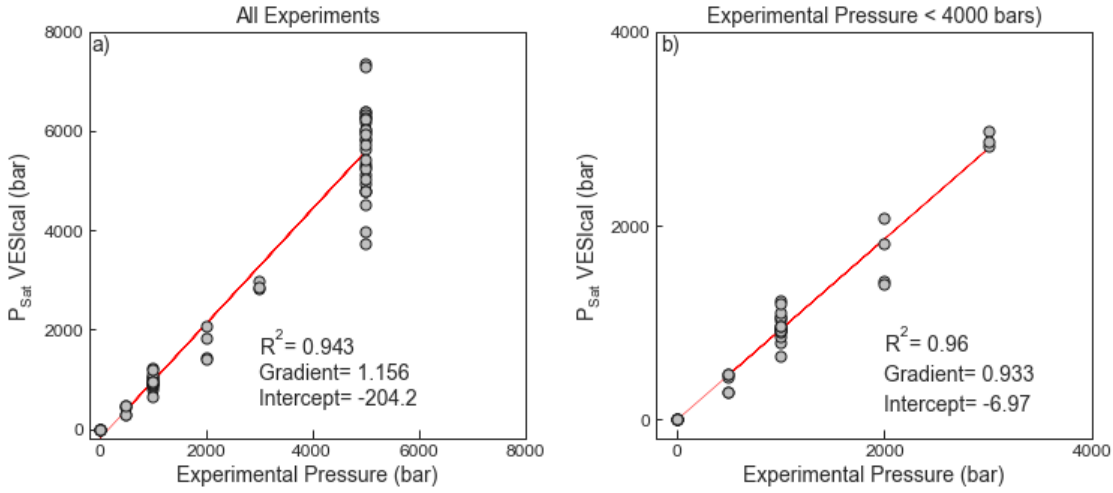
- We show the regression for experimental pressure vs. saturation pressure calculated in VESIcal for all data, and data with experimental pressures <4000 bars (to remove the most scattered datapoints).

[5]:
```
myfile_Comb = v.BatchFile('S7_Testing_Shishkina_et_al_2014.xlsx',␣
↪sheet_name='Table2_Text') # Loads experimental data from Table 2
satPs_wtemps_Shish_Comb= myfile_Comb.
↪calculate_saturation_pressure(temperature="Temp",␣
↪model='ShishkinaIdealMixing') # Calculates saturation pressures for these␣
↪compositions + tempts
```

[6]:
```
######################### H2O only experiments
X_Test3b=satPs_wtemps_Shish_Comb['Press']
Y_Test3b=satPs_wtemps_Shish_Comb['SaturationP_bars_VESIcal']
mask_Test3b = (X_Test3b>-1) & (Y_Test3b>-1) # This gets rid of Nans
X_Test3bnoNan=X_Test3b[mask_Test3b].values.reshape(-1, 1)
```

```
Y_Test3bnoNan=Y_Test3b[mask_Test3b].values.reshape(-1, 1)
lr=LinearRegression()
lr.fit(X_Test3bnoNan,Y_Test3bnoNan)
Y_pred_Test3b=lr.predict(X_Test3bnoNan)

fig, (ax1, ax2) = plt.subplots(1,2, figsize=(12,5)) # adjust dimensions of␣
↪figure here

ax1.plot(X_Test3bnoNan,Y_pred_Test3b, color='red', linewidth=0.5, zorder=1) #␣
↪This plots the best fit line
ax1.scatter(satPs_wtemps_Shish_Comb['Press'],␣
↪satPs_wtemps_Shish_Comb['SaturationP_bars_VESIcal'],  s=50, edgecolors='k',␣
↪facecolors='silver', marker='o', zorder=5)
# This bit plots the regression parameters on the graph
I='Intercept= ' + str(np.round(lr.intercept_, 1))[1:-1]
G='Gradient= '  + str(np.round(lr.coef_, 3))[2:-2]
R='R$^2$= ' +  str(np.round(r2_score(Y_Test3bnoNan, Y_pred_Test3b), 3))

ax1.text(3000, 1500, R, fontsize=14)
ax1.text(3000, 1000, G, fontsize=14)
ax1.text(3000, 500, I,  fontsize=14)

#################  CO2 experiments

X_Test3=satPs_wtemps_Shish_Comb['Press']
Y_Test3=satPs_wtemps_Shish_Comb['SaturationP_bars_VESIcal']
mask_Test3 = (X_Test3>-1) & (Y_Test3>-1) &(X_Test3<4000) # This gets rid of Nans
X_Test3noNan=X_Test3[mask_Test3].values.reshape(-1, 1)
Y_Test3noNan=Y_Test3[mask_Test3].values.reshape(-1, 1)
lr=LinearRegression()
lr.fit(X_Test3noNan,Y_Test3noNan)
Y_pred_Test3=lr.predict(X_Test3noNan)
ax2.plot(X_Test3noNan,Y_pred_Test3, color='red', linewidth=0.5, zorder=1) #␣
↪This plots the best fit line
ax2.scatter(satPs_wtemps_Shish_Comb['Press'],␣
↪satPs_wtemps_Shish_Comb['SaturationP_bars_VESIcal'],  s=50, edgecolors='k',␣
↪facecolors='silver', marker='o', zorder=5)
# This bit plots the regression parameters on the graph
I='Intercept= ' + str(np.round(lr.intercept_, 2))[1:-1]
G='Gradient= '  + str(np.round(lr.coef_, 3))[2:-2]
R='R$^2$= ' +  str(np.round(r2_score(Y_Test3noNan, Y_pred_Test3), 2))

ax2.text(2000, 100, I, fontsize=14)
ax2.text(2000, 400, G, fontsize=14)
ax2.text(2000, 700, R, fontsize=14)
```

```
ax1.set_xlabel('Experimental Pressure (bar)', fontsize=14)
ax1.set_ylabel('P$_{Sat}$ VESIcal (bar)', fontsize=14)
ax2.set_xlabel('Experimental Pressure (bar)', fontsize=14)
ax2.set_ylabel('P$_{Sat}$ VESIcal (bar)', fontsize=14)
ax1.set_xticks([0, 2000, 4000, 6000, 8000, 10000])
ax1.set_yticks([0, 2000, 4000, 6000, 8000, 10000])
ax2.set_xticks([0, 2000, 4000, 6000, 8000, 10000])
ax2.set_yticks([0, 2000, 4000, 6000, 8000, 10000])
ax1.set_xlim([-200, 8000])
ax1.set_ylim([-200, 8000])
ax2.set_xlim([-200, 4000])
ax2.set_ylim([-200, 4000])
plt.subplots_adjust(left=0.125, bottom=None, right=0.9, top=None, wspace=0.3,␣
↪hspace=None)

ax1.text(-150, 7600, 'a)', fontsize=14)
ax2.text(-150, 3800, 'b)', fontsize=14)
ax1.set_title('All Experiments',  fontsize=14)
ax2.set_title('Experimental Pressure < 4000 bars)',  fontsize=14)

fig.savefig('Shishkina_Test3.png', transparent=True)
```



1.3 Test 4 - Intepretation of "atomic fractions of cations in Equation 9. - We can only recreate the chemical data for cation fractions shown in their Fig. 7a if the"atomic fractions of cations" are calculated excluding volatiles. Including atomic proportions including H_2O and CO_2 results in a significantly worse fit to experimental data for the ShishkinaWater model shown in test 2. The choice of normalization doesn't affect the results for the CO_2 model, where the compositional dependence is expressed as a fraction

[7]:
```
# Removed CO2 and H2O
oxides = ['SiO2', 'TiO2', 'Al2O3', 'Fe2O3', 'Cr2O3', 'FeO', 'MnO', 'MgO',␣
 ↪'NiO', 'CoO', 'CaO', 'Na2O', 'K2O', 'P2O5']
oxideMass = {'SiO2': 28.085+32, 'MgO': 24.305+16, 'FeO': 55.845+16, 'CaO': 40.
 ↪078+16, 'Al2O3': 2*26.982+16*3, 'Na2O': 22.99*2+16,
                         'K2O': 39.098*2+16, 'MnO': 54.938+16, 'TiO2': 47.
 ↪867+32, 'P2O5': 2*30.974+5*16, 'Cr2O3': 51.996*2+3*16,
                         'NiO': 58.693+16, 'CoO': 28.01+16, 'Fe2O3': 55.
 ↪845*2+16*3}
CationNum = {'SiO2': 1, 'MgO': 1, 'FeO': 1, 'CaO': 1, 'Al2O3': 2, 'Na2O': 2,
                         'K2O': 2, 'MnO': 1, 'TiO2': 1, 'P2O5': 2, 'Cr2O3': 2,
                         'NiO': 1, 'CoO': 1, 'Fe2O3': 2}
```

[8]:
```
Normdata = myfile_H2O.get_data(normalization="additionalvolatiles")
```

[9]:
```
for ind,row in Normdata.iterrows():
    for ox in oxides:
        Normdata.loc[ind, ox + 'molar']=((row[ox]*CationNum[ox])/oxideMass[ox])␣
 ↪# helps us get desired column name with its actual name, rather than its␣
 ↪index. If by number, do by iloc.
        #oxide_molar[ind, ox]=ox+'molar'
    Normdata.loc[ind,'sum']=sum(Normdata.loc[ind, ox+'molar'] for ox in oxides)
    for ox in oxides:
        Normdata.loc[ind, ox + 'norm']=Normdata.loc[ind, ox+'molar']/Normdata.
 ↪loc[ind, 'sum']
            # helps us get desired column name with its actual name, rather␣
 ↪than its index. If by number, do by iloc.
Normdata.head()
```

[9]:

	SiO2	TiO2	Al2O3	Fe2O3	Cr2O3	FeO	MnO	\
1	50.175018	0.920092	18.281828	0.0	0.0	9.370937	0.170017	
2	50.175018	0.920092	18.281828	0.0	0.0	9.370937	0.170017	
3	46.237383	2.700445	14.656611	0.0	0.0	11.751120	0.164913	
4	47.327420	2.353128	14.179890	0.0	0.0	10.825606	0.173174	
5	43.666155	2.638655	12.659386	0.0	0.0	11.548572	0.195076	

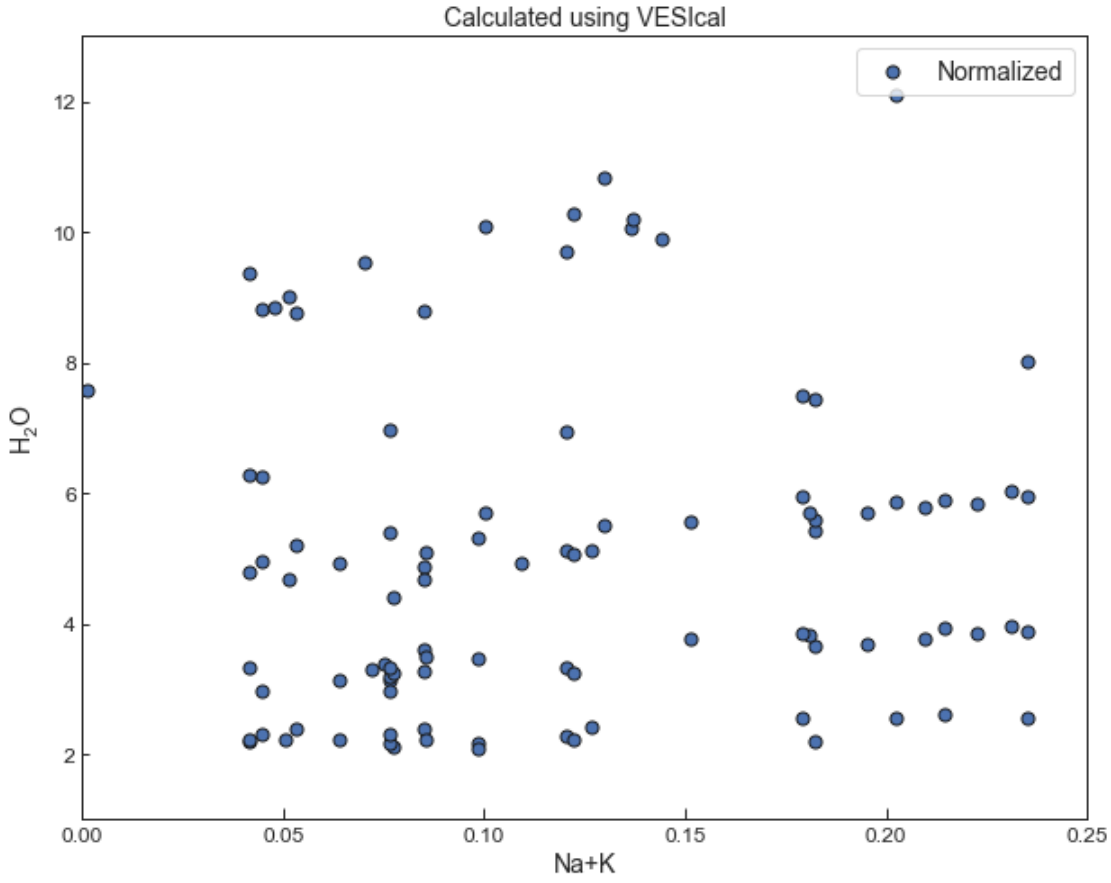
	MgO	NiO	CoO	…	Cr2O3norm	FeOnorm	MnOnorm	MgOnorm	NiOnorm	\
1	7.000700	0.0	0.0	…	0.0	0.072597	0.001334	0.096675	0.0	
2	7.000700	0.0	0.0	…	0.0	0.072597	0.001334	0.096675	0.0	

```
3   8.719756  0.0  0.0  …        0.0  0.090539  0.001287  0.119756      0.0
4  10.370063  0.0  0.0  …        0.0  0.082744  0.001341  0.141287      0.0
5  12.074159  0.0  0.0  …        0.0  0.087732  0.001501  0.163502      0.0

   CoOnorm   CaOnorm  Na2Onorm   K2Onorm  P2O5norm
1      0.0  0.112861  0.041851  0.002718  0.001176
2      0.0  0.112861  0.041851  0.002718  0.001176
3      0.0  0.104996  0.062780  0.012477  0.004341
4      0.0  0.097358  0.062455  0.009739  0.003626
5      0.0  0.115116  0.064915  0.011660  0.005369

[5 rows x 48 columns]
```

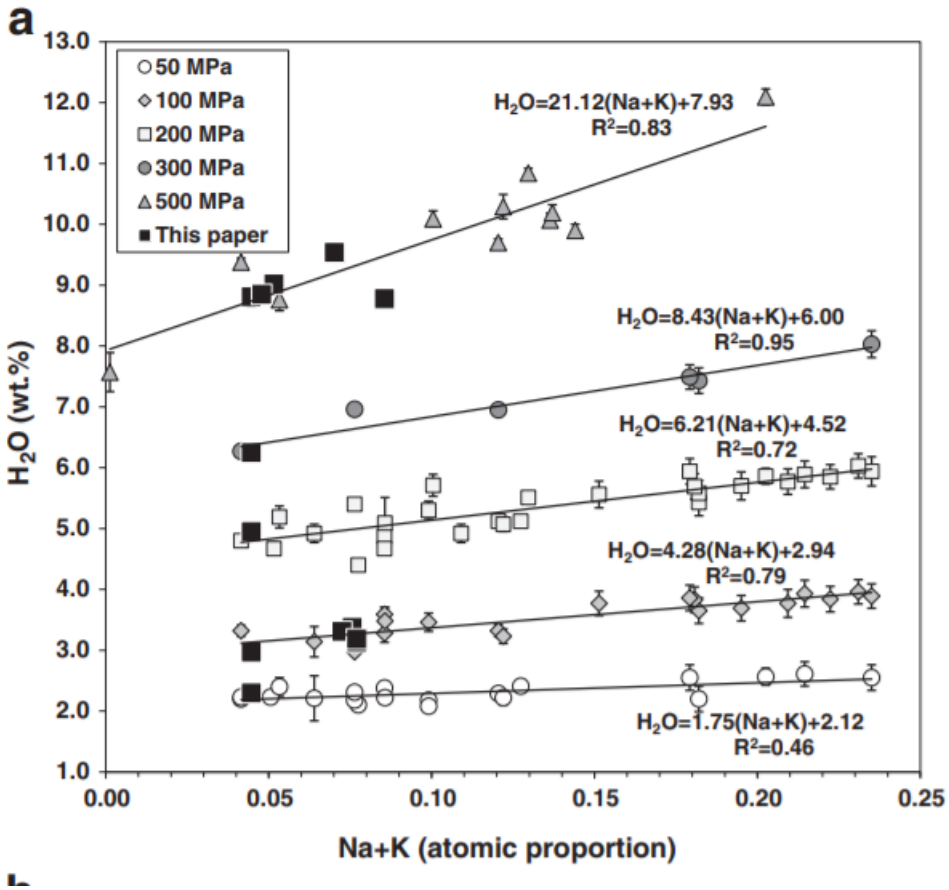
[10]:
```
### Comparison of these cation fractions to those shown in their Fig. 7a
```

[11]:
```
fig, ax1 = plt.subplots(figsize = (10,8)) # adjust dimensions of figure here
font = {'family': 'sans-serif',
        'color':  'black',
        'weight': 'normal',
        'size': 20,
        }
plt.xlim([0, 0.25])
plt.ylim([1, 13])
plt.title('Calculated using VESIcal')
plt.scatter(Normdata['Na2Onorm']+Normdata['K2Onorm'], Normdata['H2O'],␣
↪edgecolor='k', facecolor='b', s=50, label='Normalized')
plt.xlabel('Na+K')
plt.ylabel('H$_2$O')
plt.legend()
```

[11]:
```
<matplotlib.legend.Legend at 0x7fd37e3c2f90>
```


Calculated using VESIcal
Normalized
H_2O
Na+K
0.00
0.05
0.10
0.15
0.20
0.25
2
4
6
8
10
12

2 Their graph below



[ ]: