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An in situ experimental setup for Raman Spectroscopy of volatile elements in high pressure-high temperature fluids

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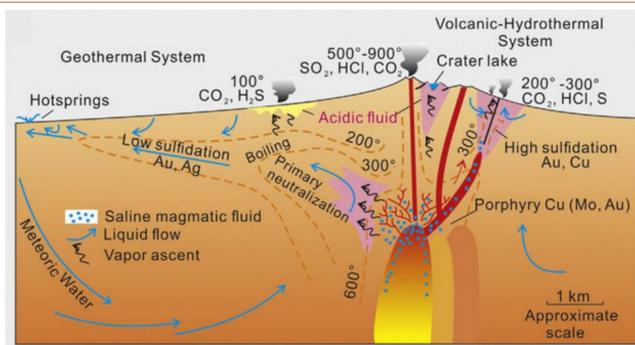
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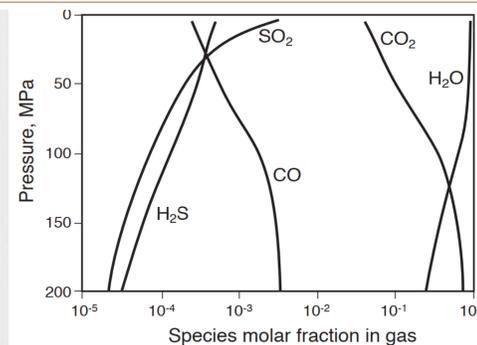
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INTRODUCTION :

Magmatic degassing is a process crucial to ore formation and with considerable environmental impact. In this context, major volatile species (H_2O , CO_2 , Cl , S , $N...$) and toxic ones (i.e. Se , $Hg...$) are released from their source in either magmatic fluids or gases (Sparks, 2003; Halter and Webster, 2004; Mason et al. 2021). Volatile degassing depends on the combined effects of temperature, pressure, melt composition and redox conditions. Since the sampling of surface gases does not acknowledge the actual volatile composition in depth, the development of in situ experimentation is essential to characterize high-pressure and high-temperature fluids in terms of speciation and partitioning.



Relationship between porphyry and epithermal ore deposits, highlighting the different metals and volatile species exsolved during magmatic degassing (Sun et al. 2015, modified from Hedenquist and Lowenstern, 1994)

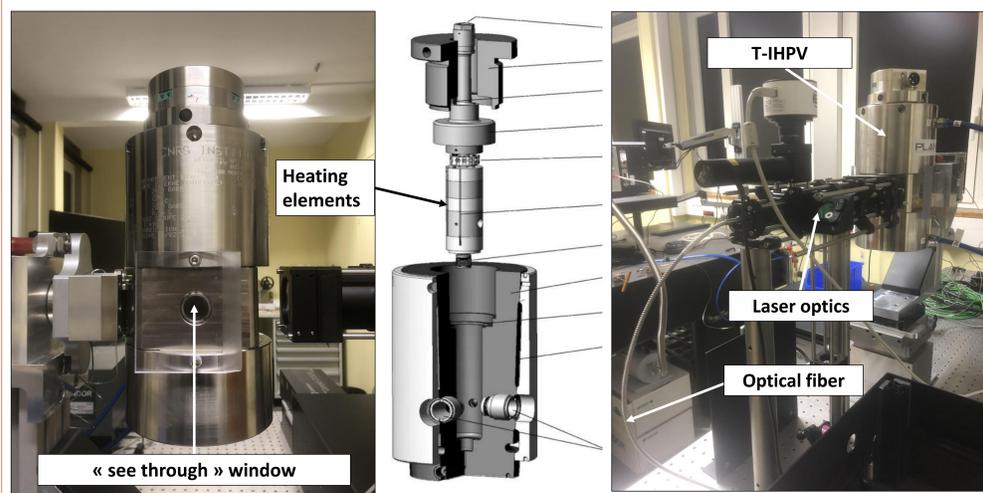


Calculated exsolved volatile phases of a degassing Mount Etna basalt at 1000°C (Audétat and Edmonds, 2020)

IN SITU APPARATUS: The « see-through » internally heated pressure vessel (T-IHPV).

The dispositive used is an updated version of an existing autoclave developed to perform measurements in supercritical fluid samples at HP-HT conditions (Testemale et al. 2005). It presents those characteristics :

- Pressure (He) is controlled to ± 1 bar by a high-P compressor system. It enables the release of extra pressure due to heating thanks to electronic valves (Bruyère et al. 2008). The maximum pressure that can be theoretically reached is up to **2000 bars**.
- Heating is achieved up to **900°C** by a furnace constituted of Mo wires wrapped coil-around a Mo transmitting tube and isolated by alumina tubes, cement and ceramics. It is controlled by a set of 2 power supplies and read to $\pm 1^\circ C$ by a thermocouple placed within the Mo transmitting tube.
- The vessel is equipped with **3 sapphire windows** surrounding the sample allowing the Raman laser beam to be transmitted through.

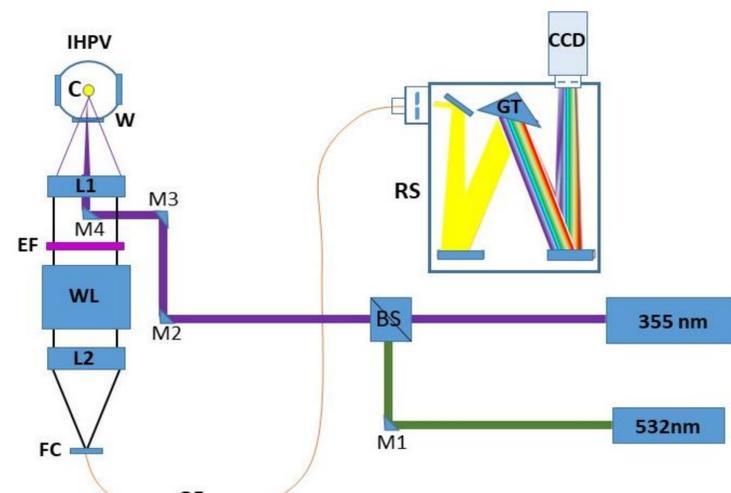


Principal components of the HP-HT pressure vessel (Testemale et al. 2005)

RAMAN SPECTROSCOPY SETUP : Principal aspects

The Raman setup has been developed by the conjoined work of ISTO and CEMHTI laboratories, with ISTO involved in the development of the experimental set-up and CEMHTI in the building of the Raman probe and focusing system.

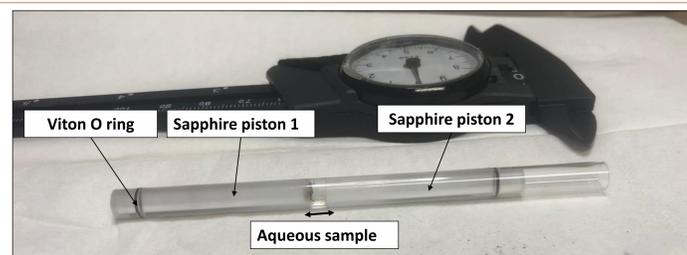
- Raman measurements can be made with 2 lasers at different wavelengths : **355 nm** (UV Coherent Genesis CX355-100 SLM) and **532 nm** (VIS Genesis MX533-500 SLM).
- The system is built with a specific optical combination of mirrors (**M1 to M4**) to select the wavelength and focus the beam on the sample (**C**) located in the « see through » internally heated pressure vessel (**IHPV**) through the sapphire window (**W**).
- The scattered signal is carried by an optical fiber (**OF**) right down to the Raman spectrometer (**RS** Andor Shamrock 500i) equipped with a back illuminated iDus CCD Detector (**CCD**).
- Raman signal can be monitored throughout the experiments and visualization can be made in real time on a computer with the Andor Solis software package.
- The Raman laser spot is approximately 100 μm (MacroRaman).



Scheme representing all the components for the Raman spectroscopy dispositive used (Slodczyk et al. under revision)

SAMPLE LOADING : The sapphire internal cell :

- Liquid samples are loaded within a specifically designed 100 mm long and 5 mm diameter sapphire internal cell. Sapphire has been chosen because it is a transparent material allowing Raman spectroscopy scattering through the sample and it is resistant to HP and chemically inert to HT.
- The sample in the cell is sealed hermetically with 2 sapphire pistons with Viton O-rings to prevent leaking during P-T increase and the consequent volume increase.
- The sapphire cell allows for relatively large sample size (ml^3 or mm^3).



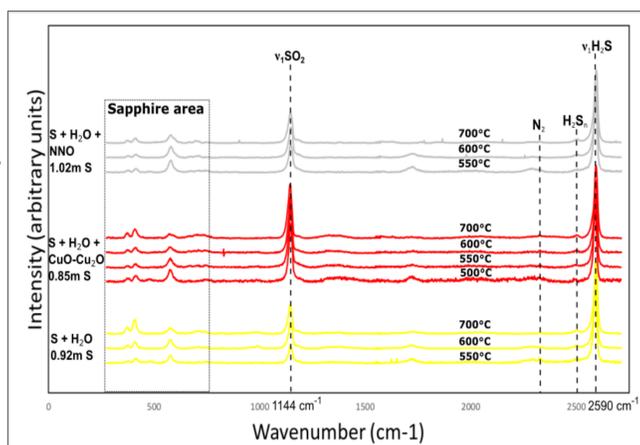
Components of the sapphire internal cell

EXPERIMENTAL EXAMPLES : speciation of S and Se in magmatic fluids

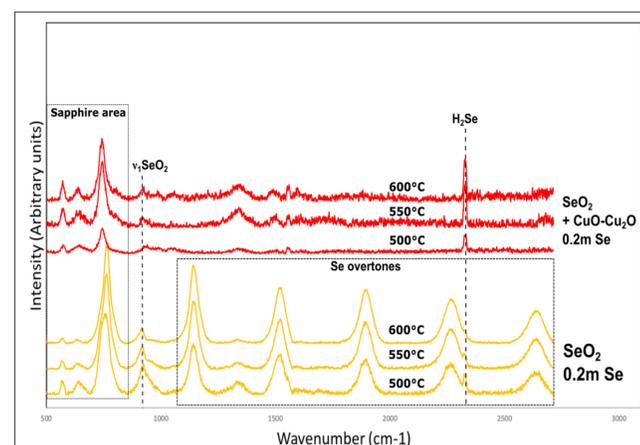
Speciation of S and Se has been investigated in 2 different aqueous S and Se-bearing solutions with mineral buffers to achieve oxygen fugacity conditions (fO_2) of NNO (mildly oxidized) and Cu_2O/CuO (oxidized) common within arc magma settings.

Preliminary results indicate a strong influence of the redox conditions on the speciation of both S and Se highlighted by the different peaks and the general shapes of Raman spectra. For instance, S appears to have strongest and more intense SO_2 oxidized species with more oxidized conditions as given by the calculated SO_2/H_2S (in between 0,8 and 1 implying that there is just as much exsolved SO_2 than H_2S).

The Raman spectra of the SeO_2 solutions presents strong differences with varying fO_2 buffers. Unbuffered conditions display overtones while it is not the case with oxidized conditions where the soles H_2Se/SeO_2 species are visible.



Speciation of S in a water solution with a chunk of elemental sulfur with varying fO_2 conditions.



Speciation of Se in a 0.2m SeO_2 aqueous solution with varying fO_2 conditions.

REFERENCES

Bruyère, R., Prat, A., Goujon, C., & Hazemann, J. L. (2008, July). A new pressure regulation device using high pressure isolation valves. In *Journal of Physics: Conference Series* (Vol. 121, No. 12, p. 122003). IOP Publishing.
 Halter, W. E., & Webster, J. D. (2004). The magmatic to hydrothermal transition and its bearing on ore-forming systems. *Chemical Geology*, 210(1-4), 1-6.
 Hedenquist, J. W., & Lowenstern, J. B. (1994). The role of magmas in the formation of hydrothermal ore deposits. *Nature*, 370(6490), 519-527.
 Mason, E., Wieser, P. E., Liu, E. J., Edmonds, M., Hyinskaya, E., Whitty, R. C., ... & Oppenheimer, C. (2021). Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kilauea Volcano, Hawaii. *Communications Earth & Environment*, 2(1), 79.
 Slodczyk et al. (under revision) *Journal of Raman Spectroscopy*.
 Sparks, R. S. J. (2003). Dynamics of magma degassing. *Geological Society, London, Special Publications*, 213(1), 5-22.
 Sun, W., Huang, R. F., Li, H., Hu, Y. B., Zhang, C. C., Sun, S. J., ... & Ling, M. X. (2015). Porphyry deposits and oxidized magmas. *Ore Geology Reviews*, 65, 97-131.
 Testemale, D., Argoud, R., Geaymond, D., & Hazemann, J. L. (2005). High pressure/high temperature cell for x-ray absorption and scattering techniques. *Review of Scientific Instruments*, 76(4), 043905

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