

**Quantitative analysis of selenium in silicate samples : development of
LA-ICP-MS methods and application to melt inclusions**

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1 Abstract

Selenium is among the least abundant elements within crustal rocks besides PGE, Au and Te, known to occur in concentrations low enough to be qualified as an ultra-trace element. Precise analysis of Se by common trace element analytical technique ICP-MS in such samples is hindered by matrix and plasma related interferences, which are significant due to its very low concentration. Only very high sensitive analytical techniques can deliver relevant measurements, such as TIMS. Consequently, very little attention has been given to Se, hence being scarcely studied and in turn poorly understood from a geochemical perspective. A few studies suggest that measuring Se within silicate samples with the ICP-MS is possible to a certain extent and that the element behaves as a volatile in magmas, however this remains unclear.

This work firstly aims at assessing the ability to measure Se with single quadrupole ICP-MS, secondly proposes and compares methods to analyze this element on an interference-free or interference-monitored basis with triple quadrupole ICP-MS and eventually aims to gain insights into its behavior within magmatic systems by measuring it in an array of melt inclusions. Melt inclusions hosted in clinopyroxene of the Onano eruption, Latera Volcano, Italy are analyzed for that.

Measuring Se in single quadrupole mode is limited to two isotopes Se^{77} and Se^{82} because of the presence of plasma related argon dimers interferences occurring on its two most abundant isotopes and the occurrence of matrix related isobaric interferences on the lower mass isotopes. Quantification of the interferences on mass 77 is achieved by analyzing Se free materials bearing interfering elements and relevance of these is discussed. Three different gases used in the reaction/collision at an optimal flow are tested in validity and compared in performance to measure Se most abundant isotopes Se^{78} and Se^{80} alongside Se^{77} . These constitute the three methods to measure Se in triple quadrupole mode. The best method is then used to analyze Se together with the major elements and a set of petrogenetic indicators in clinopyroxene hosted melt inclusions and the groundmass of rocks from the Onano eruption, Italy to decipher the behavior of the element in the context of an evolving magma chamber emptied upon eruption.

Results indicate that the precise measurement of Se in single quadrupole is only impacted by the occurrence of doubly-charged REE isotopes. Their large contribution to the apparent Se signal, even though being quantifiable, comes with potential errors due to being transient, which in fact prevents Se to be precisely measured.

Among different tests performed in triple quadrupole, ablation of Se-free glasses synthesized from high purity chemicals revealed the presence of a significant artificial signal caused by the ablation of the Se rich NITS610 SRM and consequent contamination in the sample introduction system. Addition of the reaction gases such as N₂O and O₂ can efficiently remove all interferences whereas the addition of H₂ increases the amount of remaining doubly-charge REE isotopes, leading to higher errors in signal contribution removal. Even though a significant drop of sensitivity is observed due to partial conversion of analyte to single oxide and kinetic energy loss, the addition of N₂O or O₂ largely decreases the backgrounds providing exceptionally low LODs.

Eventually, melt inclusions and groundmass analysis prove that Se behaves as an incompatible element in clinopyroxene, nonetheless being less incompatible than S. The primitive basanitic melt that fed the erupted part of the plumbing system contains about 200 ppb Se, the concentration subsequently increasing to almost 1 ppm owing to fractional crystallisation. The crystalline groundmass bears very little Se, ranging from 10 to 100 ppb. Data thus demonstrate that most of the Se is lost upon eruption, hence can be considered as a volatile element in magmas. These findings only apply to highly oxidising conditions +2.0-2.4 ΔNNO as Se is a heterovalent element and any variability in fO₂ regime may consequently affect its speciation and in turn its behavior.

Keywords: *Selenium · LA-ICP-MS · LA-ICP-MS/MS · interferences · igneous petrology · volatile · melt inclusion · crystalline groundmass · Onano eruption*