How extensive is the effect of Fe and S on the solubility of PGE in silicate melts?

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There have been numerous experimental studies where the solubilities of the platinum group elements (PGE) in silicate melt have been determined. The data gathered from these studies were extensively used to assist in the interpretation of early accretionary processes, and the anomalous enrichment of mantle and crustal rocks in PGE. However, mostly due to difficulties imposed by the presence of FeO, the majority of these experiments were carried out using simplified silicate melt compositions containing only CaO, SiO_2, MgO and Al_2O_3. The conspicuous absence of FeO and of S^{2-} from these silicate melt compositions renders it difficult to correlate the results of previous studies with natural silicate melts that are both iron and sulphur-bearing.

In order to investigate the effect of Fe and S on the solubility of PGE in silicate melts, a natural picrite was equilibrated with Pd and Ru at 1300°C in a 1 atm vertical gas mixing furnace, while varying both oxygen and sulphur fugacities (fO_2 and fS_2).The resulting silicate glasses were analysed for major elements and S by EMP, and for Pd by LA-ICPMS to allow for the detection of heterogeneities such as discrete nanonugguets of Pd and Ru metal.

Our early results show that Pd solubility in the melt decreases with increasing fS_2, while Ru solubility appears to increase. Moreover, even though Ru metal is known to be stable at high temperature and high fS_2 (see Bockrath *et al.* Chem. Geol. 2004) Pd is unstable in the presence of S^{2-} and promptly reacts to form a metal-rich Pd sulphide melt. Borisov and Palme (Am. Mineral. 2000) proposed that the effect of Fe on the solubility of PGE in silicate melts would be purely a function of the activity-composition relationships among Fe and the different PGE. However, our results show that with respect to Pd, the change in oxidation state of Fe^{2+} to Fe^{3+} at fO_2 larger than FMQ is coupled with a concurrent increase in the solubility of Pd in the silicate melt.

It will be demonstrated that the presence of FeO and S^{2-} has a significant effect on the solubility and speciation of Pd and Ru in silicate melts at high-temperature.

Selenium biogeochemistry as a deep-time redox proxy

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The history of Earth's environmental oxygenation is known in general terms: essentially anoxic in the Archean, passing through two rises during the Proterozoic and maintaining highly oxic conditions through the Phanerozoic. However, it is not well known how high environmental oxygen levels were between the Archean and Phanerozoic stages, if rises in oxygen levels were sudden or gradual, monotonic or incremental, foreshadowed or uniform, or whether atmospheric oxygenation changes were directly reflected by marine oxygenation and biological metabolism.

As a geochemical analog of sulfur, selenium mass-dependent isotope variations may also be a potential tracer of the redox history of Earth's environment. Selenium isotopes fractionate during biotic and abiotic redox reactions, but under different Eh conditions than sulfur. Combined with residence times in various geochemical reservoirs that constrast with sulfur, Se isotope variations through time could thus provide new and complementary constraints on environmental oxidation. As a further analogy to sulfur, it is also possible that mass-independent fractionations of Se isotopes will be discovered, potentially providing insights into Se gas cycling and atmospheric oxygen levels over time.

We have adapted a suite of recently-devised experimental methods to measure Se isotope ratios: thiol-cotton fiber to extract Se from acid-digested rock samples, continuous-flow hydride generation to selectively volatilize Se and enhance signal strength, multi-collector inductively-coupled plasma mass-spectrometry to measure Se isotopes with high sensitivity; and applied interference correction procedures in order to measure Se isotopes reliably in natural samples. Analysis of $\delta^{76/78}$Se, $\delta^{77/78}$Se and $\delta^{82/78}$Se in standards and sulfides shows a 2σ precision ≤ 0.2 ‰.

We will present results of a Se-isotope investigation of a sample suite that represents a range of geological environments, redox conditions, and ages. Combined with sulfur concentration and isotope data, we can thus evaluate the potential of a Se isotopic approach to study local and global redox transitions in Earth's history.