



	<b>Experiment title:</b> The oxidation state of vanadium in geological melts	<b>Experiment number:</b> EC-650
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 07/04/2010 to: 13/04/2010	<b>Date of report:</b> 28/02/2011
<b>Shifts:</b> 18	<b>Local contact(s):</b> Janine Grattage	<i>Received at ESRF:</i>
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## Report:

Vanadium can occur as  $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$  and the transition from  $V^{2+}$  to  $V^{5+}$  covers the entire spectrum of redox conditions observed in high-temperature geological and cosmochemical materials. As a result, the oxidation state of V (either determined directly or inferred from its relative abundance in coexisting crystals and melt) can be used as an indicator of the redox conditions under which a material formed. Redox conditions are important as they are indicative of geological settings and processes, and can provide insight into how the Earth has evolved with time

To investigate the redox chemistry of V we prepared a series of silicate glasses that are synthetic analogues of geological melts (such as basalts) over a range of oxygen fugacities ( $fO_2$ ). The oxidation state of V in these samples is expected to vary systematically from entirely  $V^{5+}$  to entirely  $V^{2+}$ . The glasses contain 0.4 wt% V, are ~5 mm in size, and were presented as polished surfaces in epoxy resin.

In previous work, V K-edge XANES spectra were recorded at the APS for over 60 samples. The  $1s \rightarrow 3d$  pre-edge appears to be the spectral feature that is most sensitive to changes in oxidation state and has been used to determine the average V valence. However, it has not been possible to distinguish between, for example,  $V^{4+}$  and a mixture of  $V^{3+}$  and  $V^{5+}$ . This severely limits our ability to understand the redox behaviour of V in melts and to test models inferring valence state from partitioning behaviour (i.e. abundance in coexisting phases). In the present experiment  $1s2p$  RIXS and  $K\beta$  spectra were recorded for a subset of these samples. The hope was that these sensitive probes of orbital structure would yield spectral features that were diagnostic of each oxidation state (as appears to be the case in some V L-edge spectra). In the K-edge spectra it is not possible to determine the abundance of four different species from the behaviour of a single peak; additional features in the RIXS place could potentially solve this problem.

RIXS planes were recorded for  $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$  standards and approximately 30 glass samples. The beamline functioned exceedingly well and was ideal for the proposed experiment. The samples studied covered the full range of V redox states, two different compositions, and included some additional glasses for which the V oxidation states had been (tentatively) determined by a combination of chemical titrations and optical absorption spectroscopy. Representative RIXS planes are shown in the Figure.

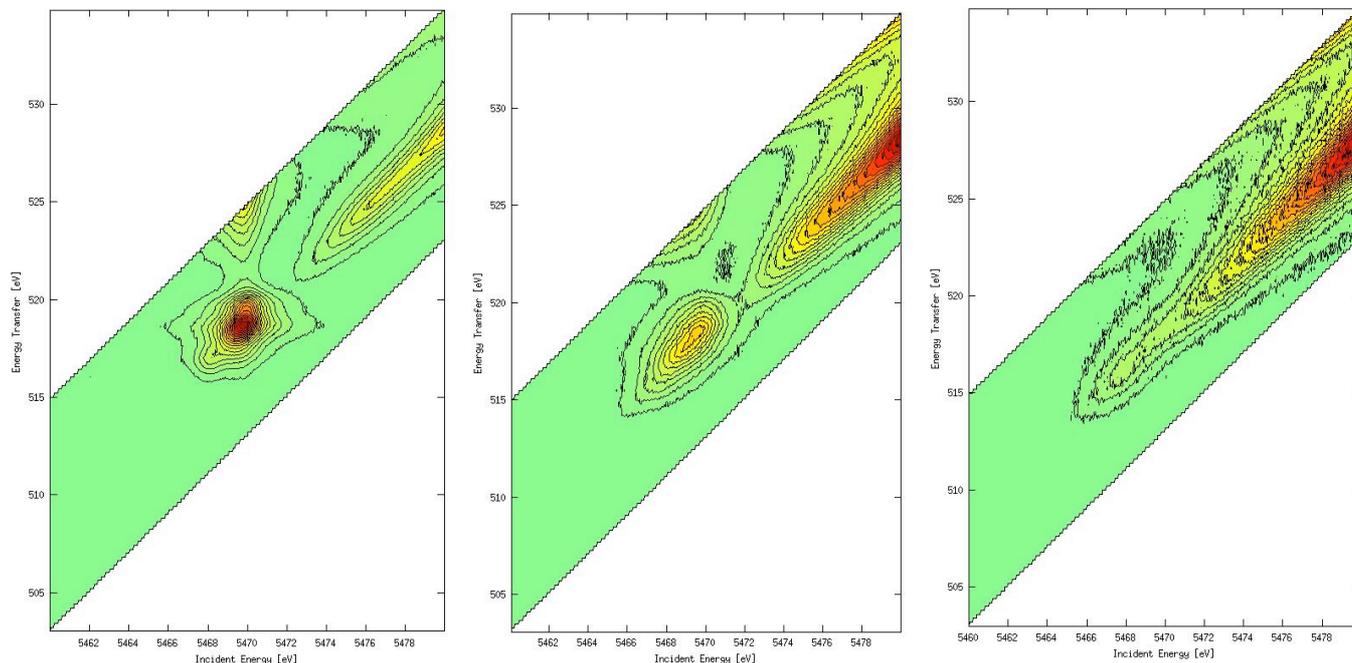


Figure: V 1s2p RIXS contour plots for glasses that were equilibrated as melts under (from left to right) progressively more reduced conditions. The sample represented by the plot on the left should predominantly contain  $V^{5+}$ , that in the centre a mixture of  $V^{4+}$  and  $V^{3+}$ , and that on the right mainly  $V^{2+}$ .

The 1s2p RIXS planes for glasses in which the V oxidation state varies systematically from  $V^{5+}$  to  $V^{2+}$  show differences, however, these are continuous. Distinct features do not appear or disappear as could occur for the appearance and disappearance of different V oxidation states. Profiles through the planes give a single lineshape that varies in intensity and energy. Attempts to model the profiles as a distribution of species is complicated by the uncertainty of the number of components that may be expected for each V valence state in poorly defined coordination environments. Further, due to a systematic broadening and decrease in intensity with decreasing valence state the error associated with any attempt at quantifying  $V^{2+}$  (and possibly  $V^{3+}$ ) will be significant. We should stress that methods for modelling RIXS are complex and still under development. We are currently attempting a type of principal component analysis using software that is normally used for modelling landforms such as mountain ranges.