Partitioning of redox sensitive elements (particularly V, Sn and Mo) in experimentally derived Rutile and Zircon mineral grains

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Objective

The aim of this study is to understand the partitioning of redox- sensitive trace elements (particularly V, Sn and Mo) in experimental zircon and rutile mineral grains using electron microscopy. Synthetic mineral grains of zircon and rutile were grown using a Boyd and London end – loaded piston cylinder in our lab at a temperature of 920°C and a pressure of 1GPa for 5 days. Multiple experiments were conducted at different redox conditions which is constrained using chemical metal-metal oxide buffers to fix our oxygen fugacity. The run products show that there is preferential incorporation of vanadium, tin and molybdenum in rutile and to a smaller extent in zircon.

Sample Preparation

The sample consisted of zircon and rutile grains which were mounted on a resin of 5-part epoxy and 1-part hardener mixture. These materials are naturally not conductive hence sputter – coating, was necessary. Initially samples were gold coated but the X-ray peak of zircon interferes with that of gold, so a carbon evaporation was chosen as the process for making a conductive layer. A continuous piece of carbon tape was also attached to the resin and to the base of the sample stub to facilitate the flow of charge.

Fig.1 : Carbon – coated epoxy mounts on sample holder of the SEM

Fig.2 : Carbon tape can be seen attached to the sample and the stub

SEM Images of Zircon and Rutile mineral grains

The grains of rutile and zircons showed a bimodal size distribution where the rutile grains are on the scale of ~ 10 μm are on the scale of ~ 5 μm. This is relatively easier for a field emission source SEM, like the one we have in the optics department to have access to. Below are the SEM images of the samples that I took in the SEM :

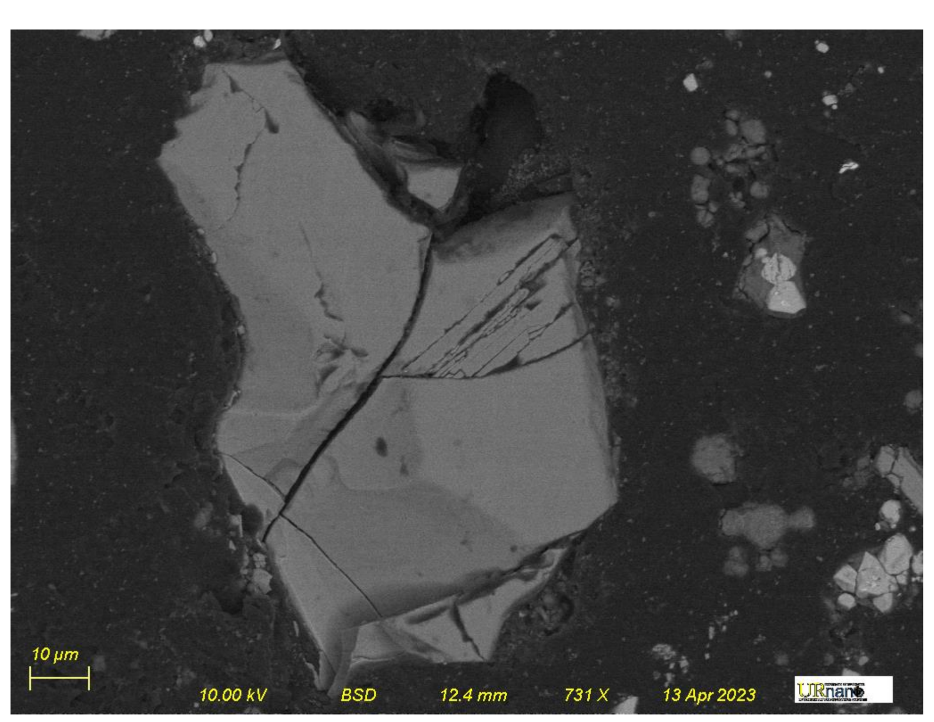


Fig.3 : Backscattered electron image of a rutile grain.

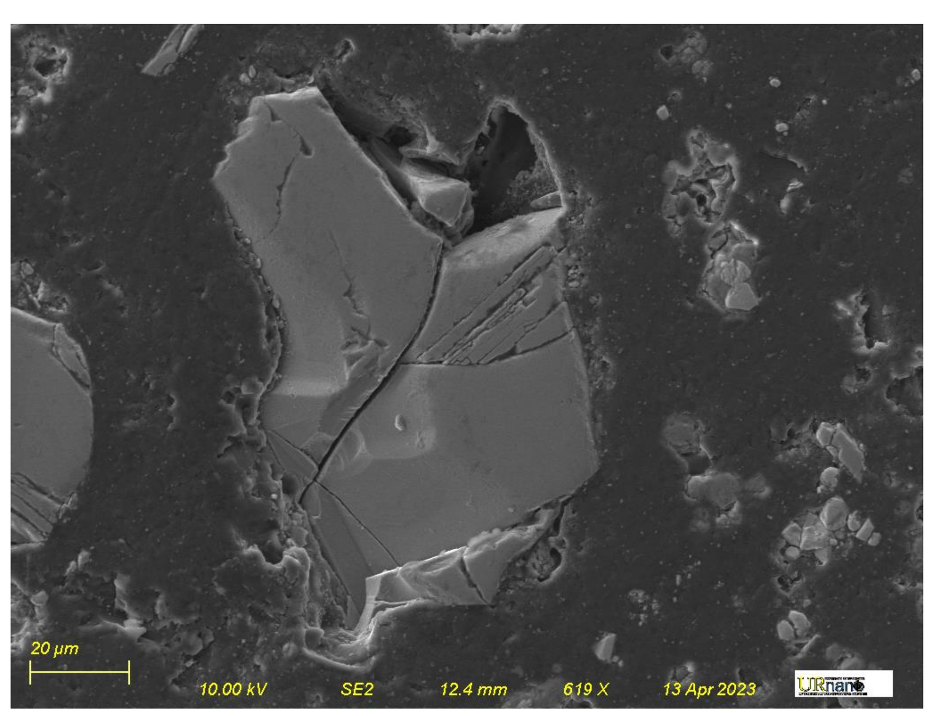


Fig.4 : Secondary electron image of the same rutile grain

Fig.5 : Back-scattered electron image of a cluster of zircon grains

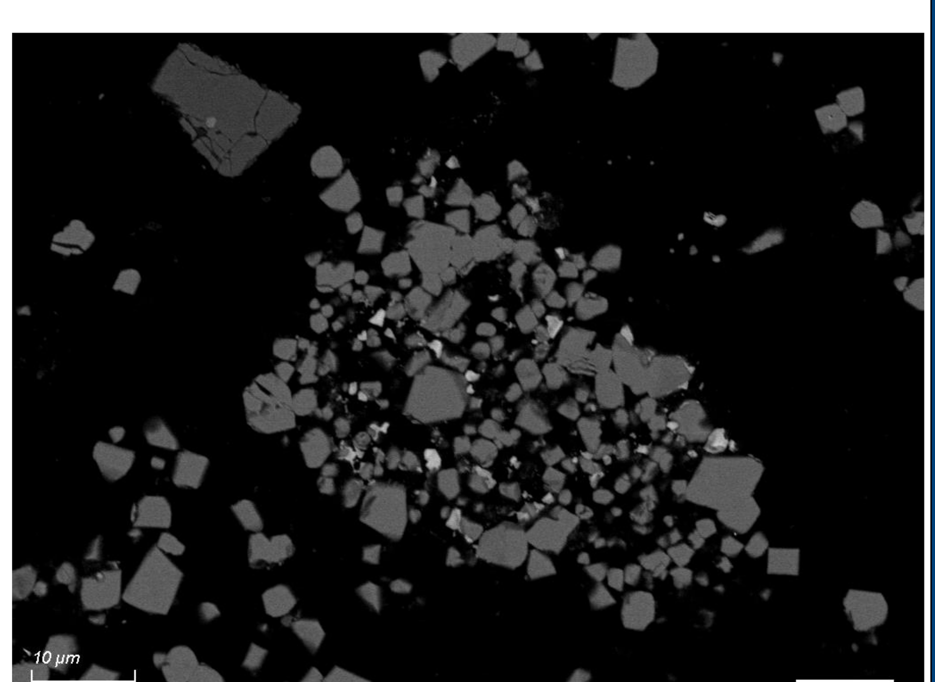
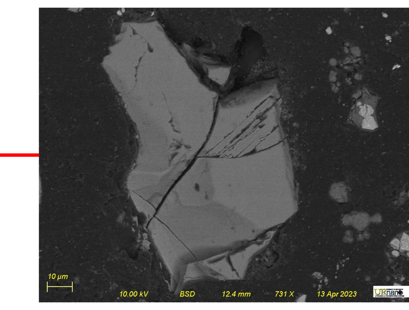


Fig.6 : Cluster of zircon grains in Backscattered imaging mode

Elemental Maps using EDS

The following X – ray EDS spectra were captured using the EDAX detector in the SEM for the rutile and the zircons mineral grains



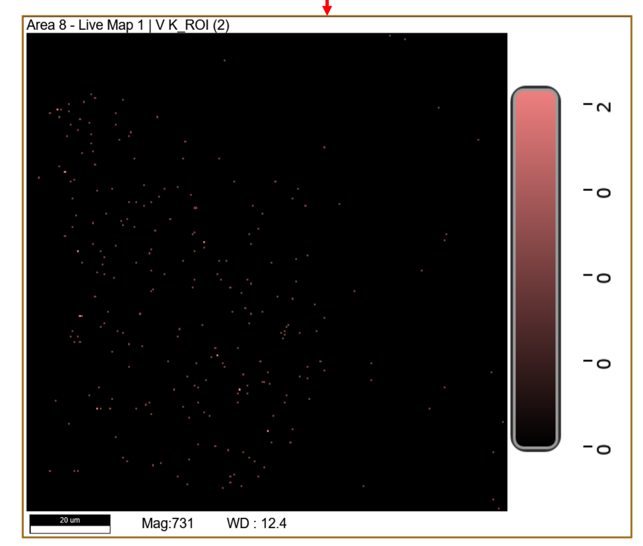


Fig.7 : Elemental map of Vanadium in Rutile

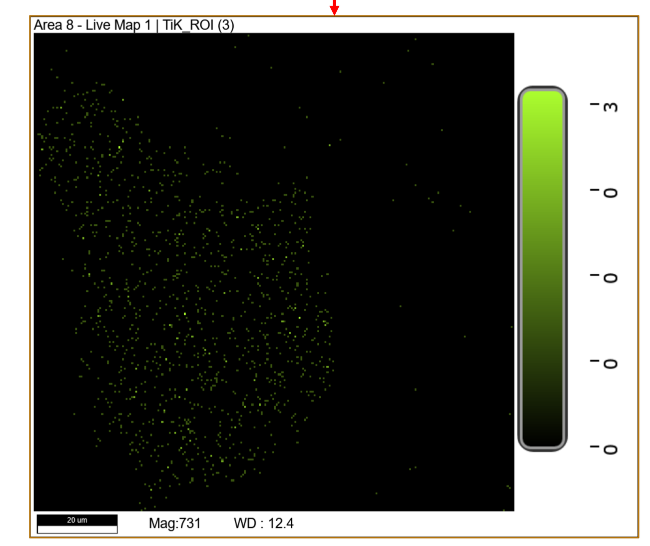


Fig.8 : Elemental map of Titanium in Rutile

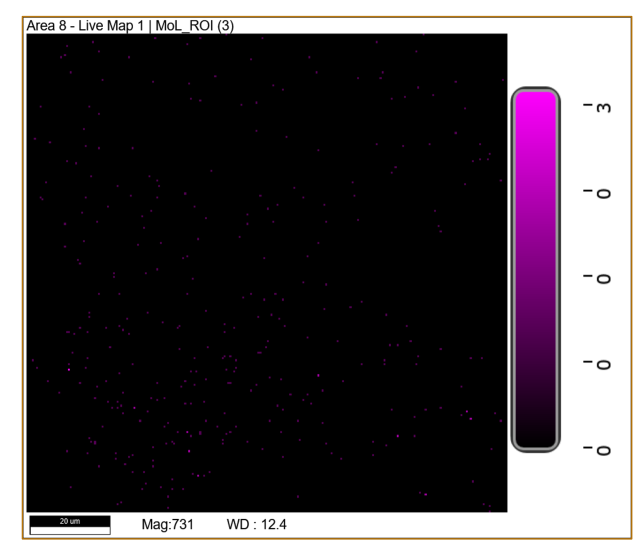


Fig.9: Elemental map of Molybdenum in Rutile

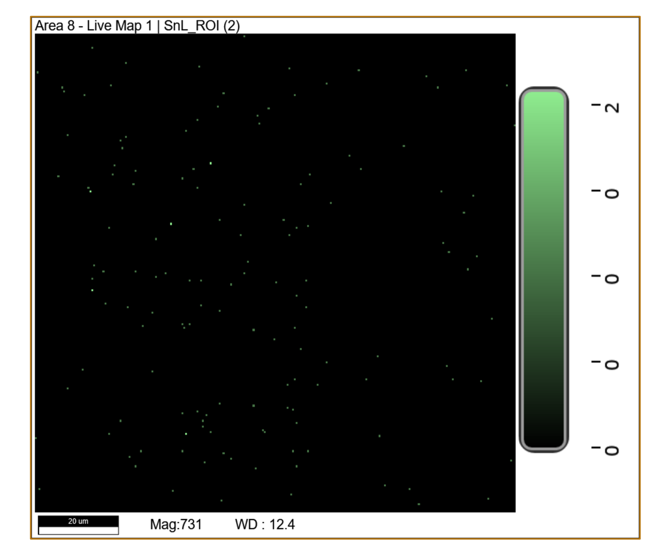
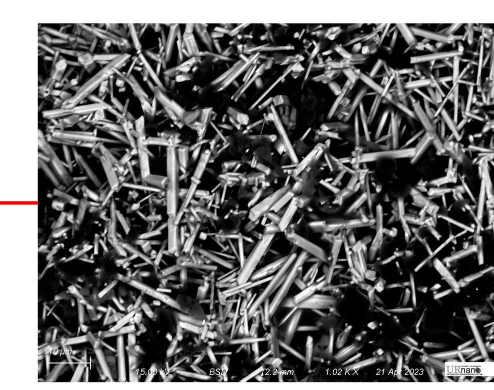


Fig.10 : Elemental map of Tin in Rutile



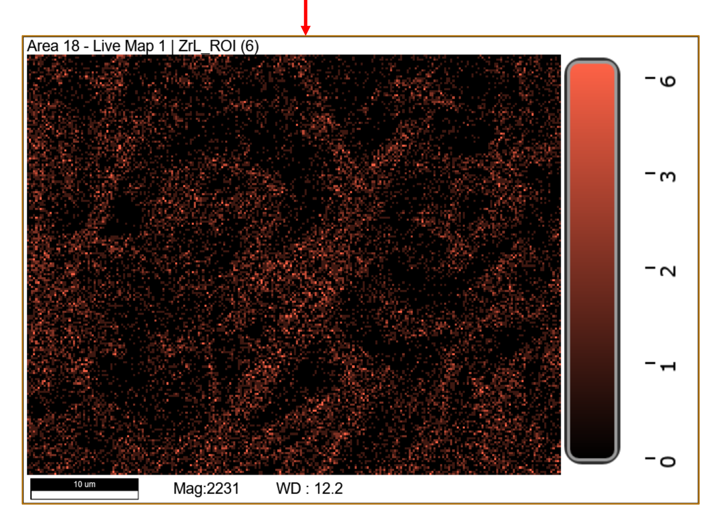


Fig.11 : Elemental map of Zirconium in Zircon

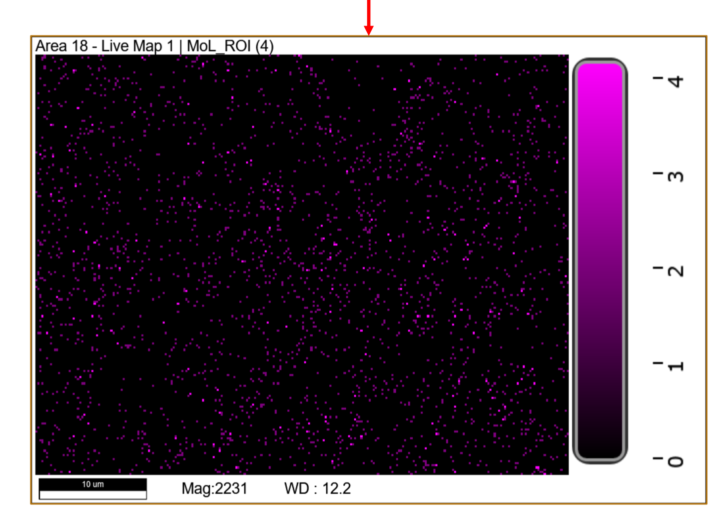


Fig12 : Elemental map of Molybdenum in Zircon

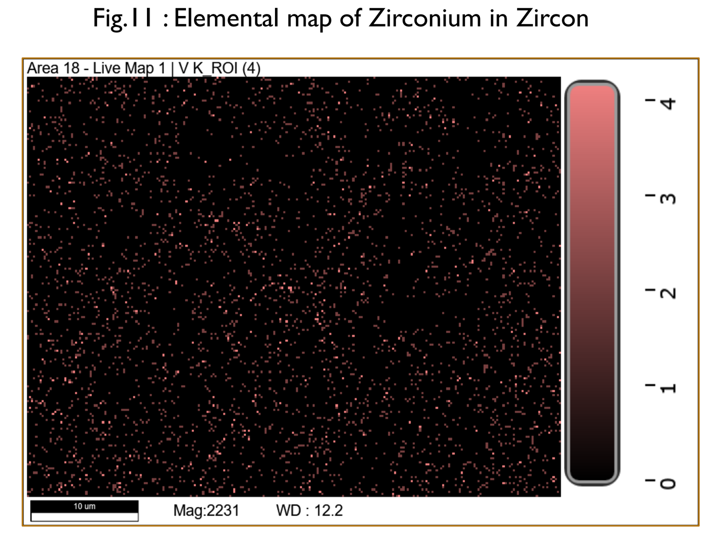


Fig.13 : Elemental map of Vanadium in Zircon

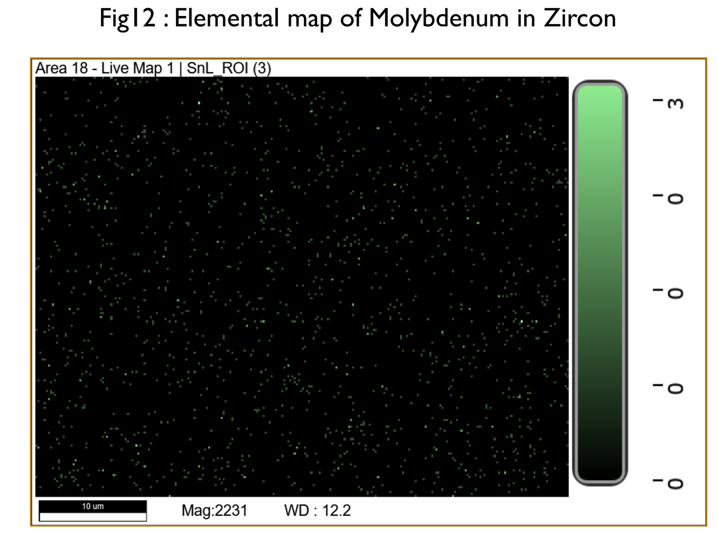


Fig.14 : Elemental map of Tin in Zircon

The above elemental maps demonstrate the presence of redox sensitive trace elements like Vanadium partitioning into rutile grain which is expected according to studies on synthetic rutile (Holycross et al., 2021). In zircon however, the opposite is true and can be observed via these elemental maps. We can attest to the presence of Molybdenum in zircon if we closely follow the pattern of the zircon grains or the zirconium map in the busy image. Similar is the case with Vanadium in zircon as rough mirroring of the zircon grains can be found when compared with the Vanadium. There is no observable presence of pattern in Tin, but it is present.

SEM Images of Zircon and Rutile clustered together

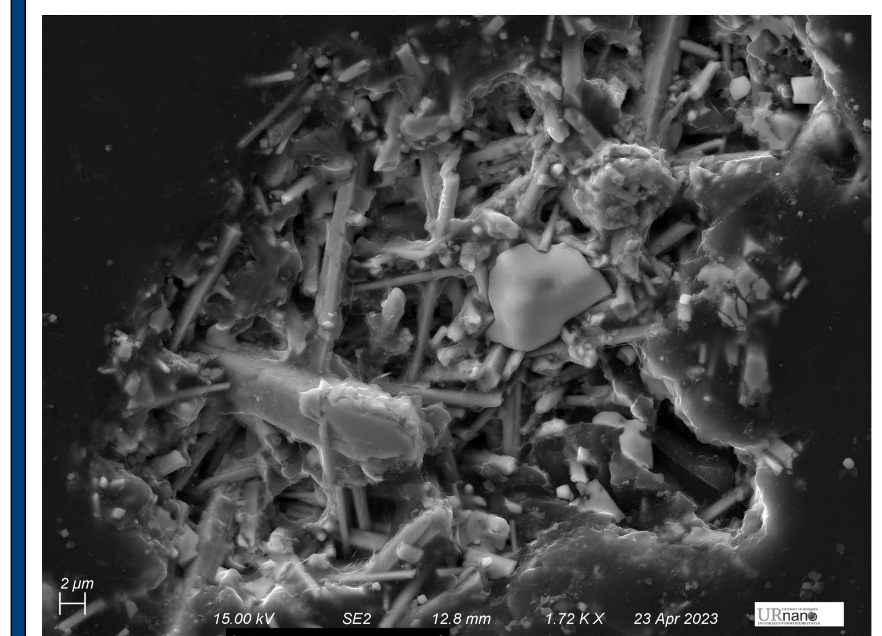


Fig.15 : Secondary electron images of a cluster of both rutile and zircon. This cluster has been created due to uneven polishing of the epoxy

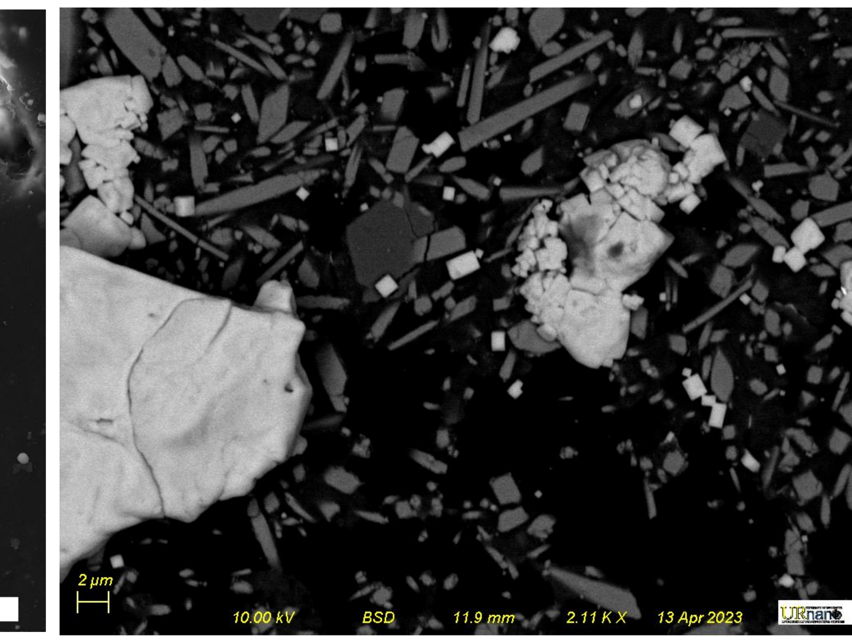


Fig.16 : Backscattered image of both rutile and zircon. The white colored particles are remnants of potassium iodide which I used to remove the gold coat which I initially sputtered.

Energy Dispersive X- Ray Spectrometry (EDS)

The following X – ray EDS spectra were captured using the EDAX detector in the SEM for the rutile and the zircons mineral grains.

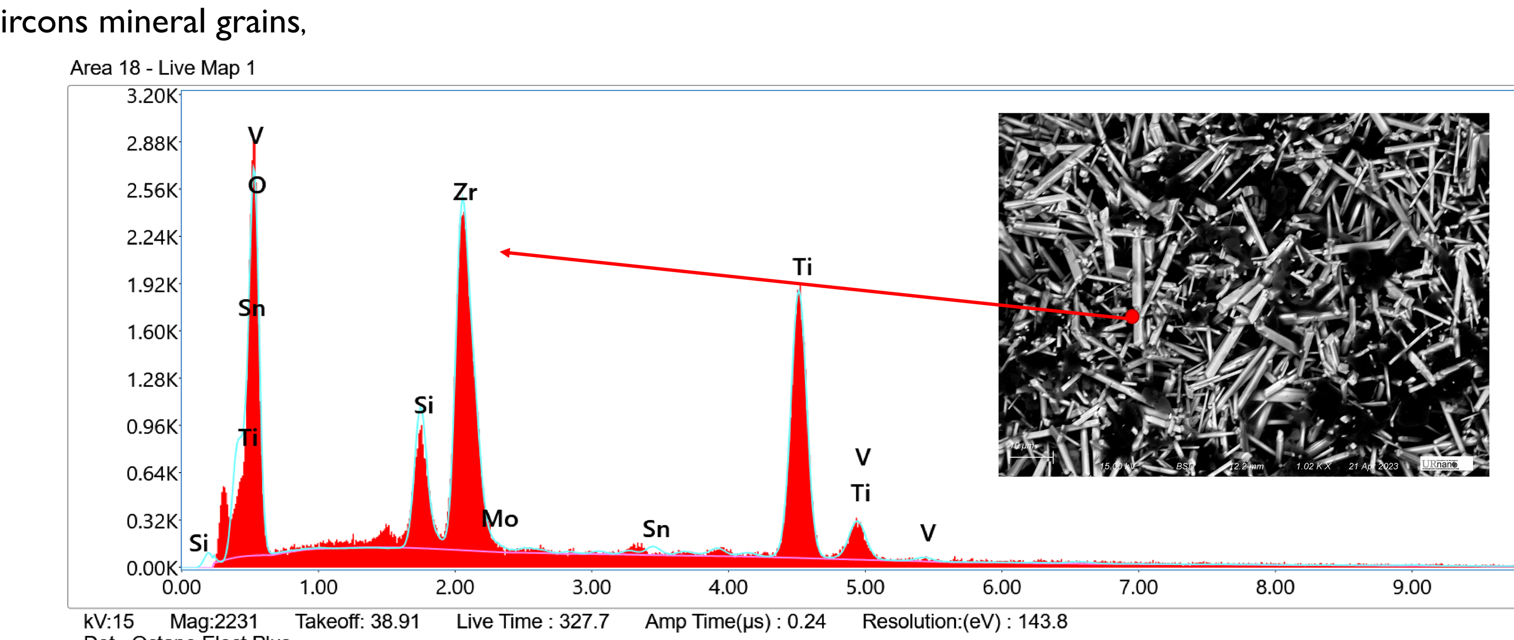


Fig.17 : EDS spectra of zircon grains in the BSE image shown before.

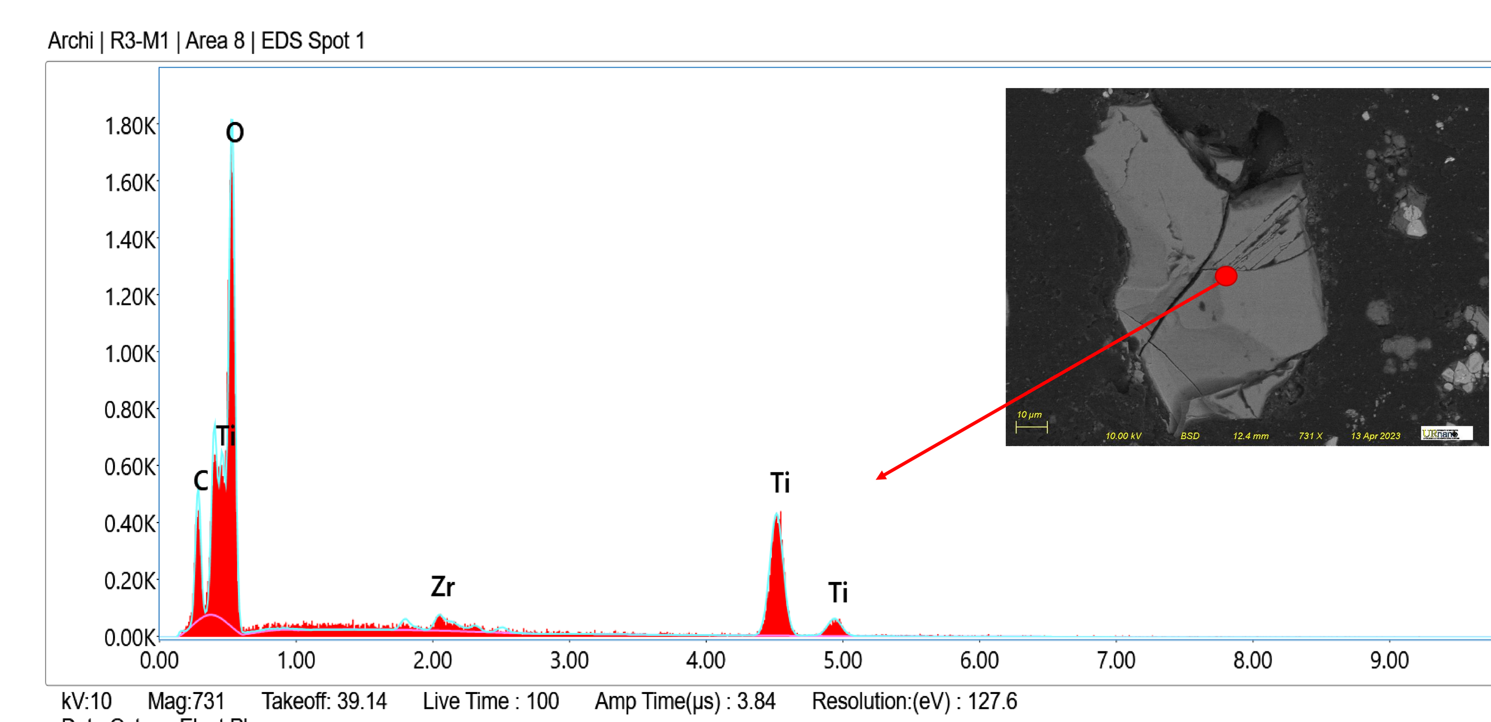


Fig.18 : EDS spectra of rutile grains in the BSE image shown before.

Inferences

- Carbon – coating is the best sputter method for geological samples containing zircon especially if EDS measurements are required.
- Back-scattered images provide better distinction between different mineral phases in comparison to Secondary electrons which show surface features better.
- There is more preferential incorporation of Vanadium in rutile as compared to Molybdenum and Tin, in that order. While in zircon, there is the presence of all the three elements and more tin than in rutile.
- The homogenous distribution of the trace elements indicate that equilibrium had been achieved and maintained throughout my experimental process.

Acknowledgements

I would like to thank Dr. Sean O' Neil, Dr. Greg Madejski and Ethan Luta for helping me with the process of learning how to use the SEM and for their continued support through all my stupid questions and inability to figure out which sputter coating works best for my sample.