

# Investigation of the interaction of water with plutonium oxide analogues

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## Introduction

Approximately 250 tonnes of separated Pu are currently stockpiled worldwide. ~50% is in interim storage in the UK whilst further processing or long-term storage options are considered.

Interim storage of PuO<sub>2</sub> involves sealing in inert steel containers under an inert atmosphere. Under certain circumstances, these gas canisters have been observed to spontaneously heat up and pressurise.

5 routes to gas production have been suggested:

- Helium accumulation from  $\alpha$  decay;
- Decomposition of polymeric packing material;
- H<sub>2</sub>O desorption (steam) from hygroscopic PuO<sub>2</sub>;
- Radiolysis of adsorbed water;
- Generation of H<sub>2</sub> by chemical reaction of PuO<sub>2</sub> with H<sub>2</sub>O, producing a postulated PuO<sub>2+x</sub> phase.

The last 3 processes all involve PuO<sub>2</sub>/H<sub>2</sub>O interactions and are complex, inter-connected and poorly understood.

## Aim

The aim of this project is to investigate the interaction of plutonium oxide (and less radioactive analogues) with water electrochemical and crystal microbalance methodologies.



## Results

Initial microbalance studies have been performed using quartz crystals coated with ceria. The temperature response of the crystal was first measured (fig. 2). For quartz, a logarithmic change in frequency with increasing temperature was observed. An alternative crystal, GaPO<sub>4</sub> was also assessed, showing a much smaller effect of temperature.

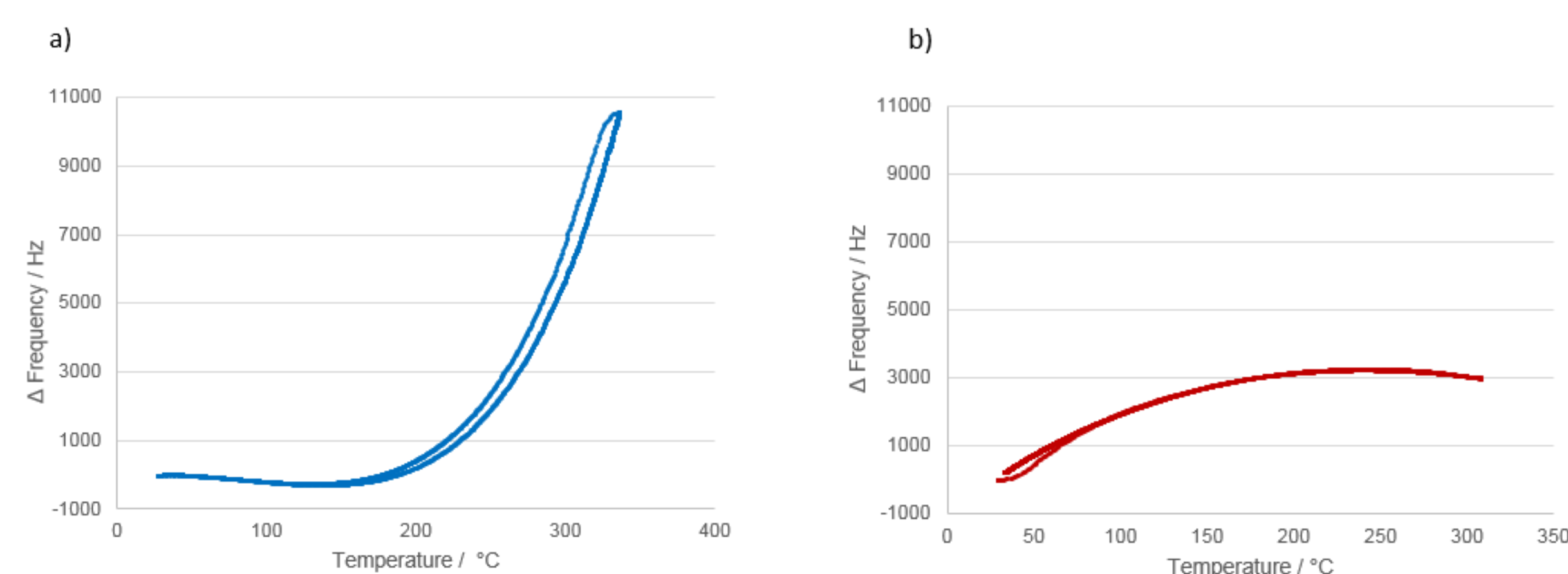


Fig. 2. Temperature dependence of uncoated a) Quartz and b) Gallium phosphate crystals, between 30 and 300°C, using high temperature QCM probe.

The two crystal types were then coated with ceria via spin coating with a cerium nitrate solution containing a polymeric surfactant. Changing the concentration of this precursor solution allowed layers of different thicknesses to be manufactured. Scanning electron microscopy was used to determine the thickness and surface area of the coatings (fig. 3).

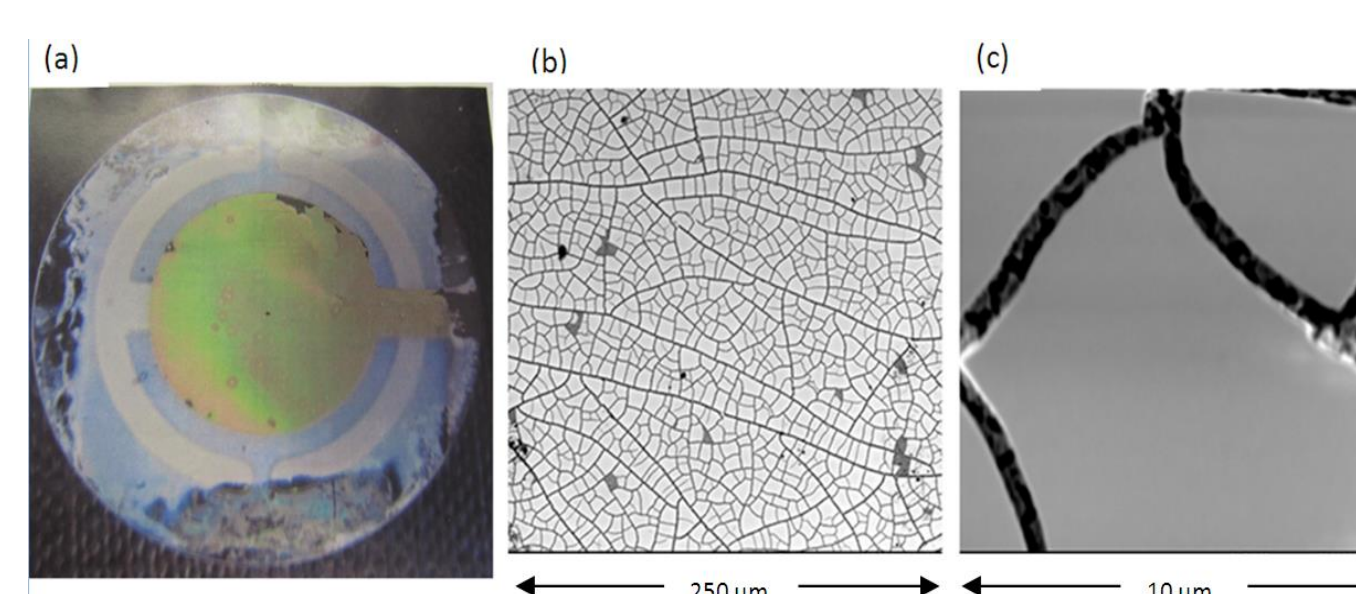


Fig. 3. Scanning electron micrographs of 400 nm thick ceria-coated quartz crystals. The ceria layers were found to be well adhered. Cyclic voltametric studies indicate the surface cracks do not penetrate to the underlying electrode material.

The resonant frequency of the coated crystals was then measured in a sealed reaction vessel in the presence of water (fig. 4), which showed that an increase in mass occurred as water was absorbed onto the ceria layer. Variation of the temperature up to ~200°C was then used, showing that the absorbed water is desorbed as the sample is heated (fig. 5).

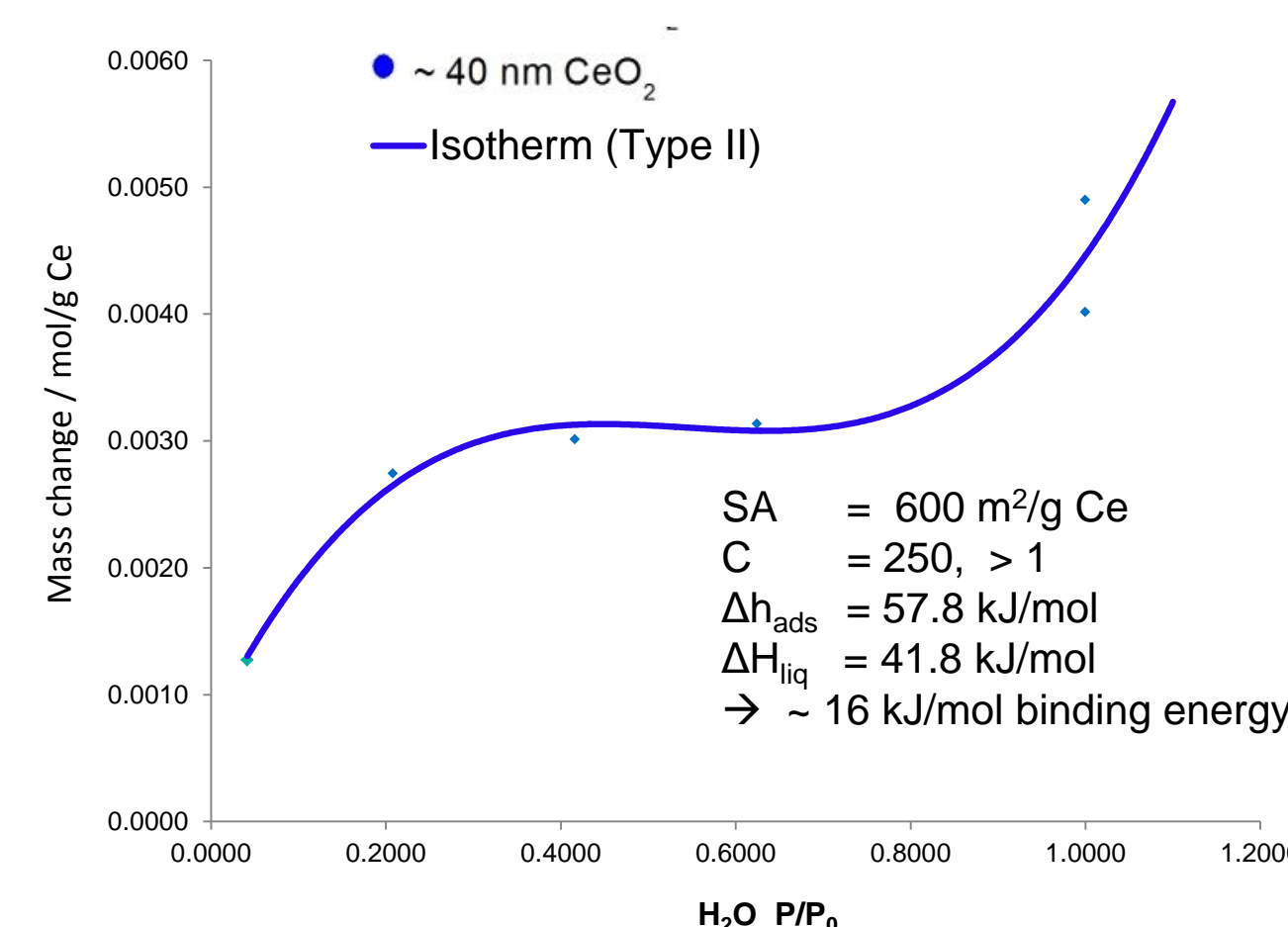


Fig. 4. Mass change due to water adsorption on 40 nm thick CeO<sub>2</sub> coated GaPO<sub>4</sub> crystals at 75°C.

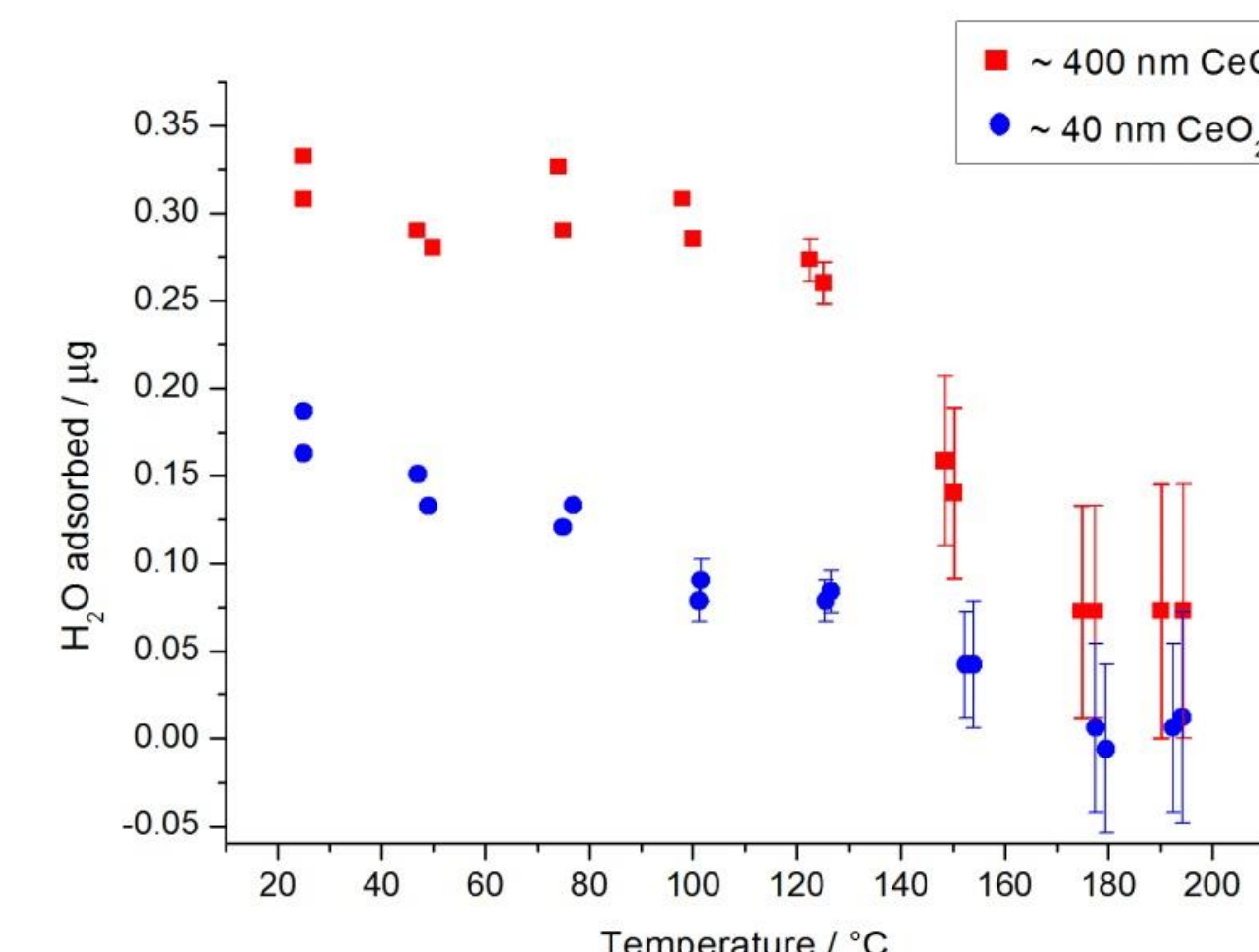


Fig. 5. Mass of water adsorbed on 40 nm and 400 nm thick CeO<sub>2</sub> coated quartz crystals from 20 to ~200°C.

## Crystal Microbalance Methodology

Crystal microbalances utilise the piezoelectric effect to accurately measure very small changes in mass of a crystal, via changes in the frequency of the crystal vibration in response to an applied current. Through coating the crystal with a thin layer of the metal oxide of interest, any changes in frequency due to absorption or desorption of gases at the oxide surface can be measured, and the change in mass determined using the Sauerbrey equation.

$$\Delta f = - \left( \frac{n f_0^2}{A \sqrt{\rho_q \mu_q}} \right) \Delta m$$

The calculated mass can then be used to determine, for example, the amount of hydrogen lost, or the number of water layers de-/absorbed onto the oxide surface.

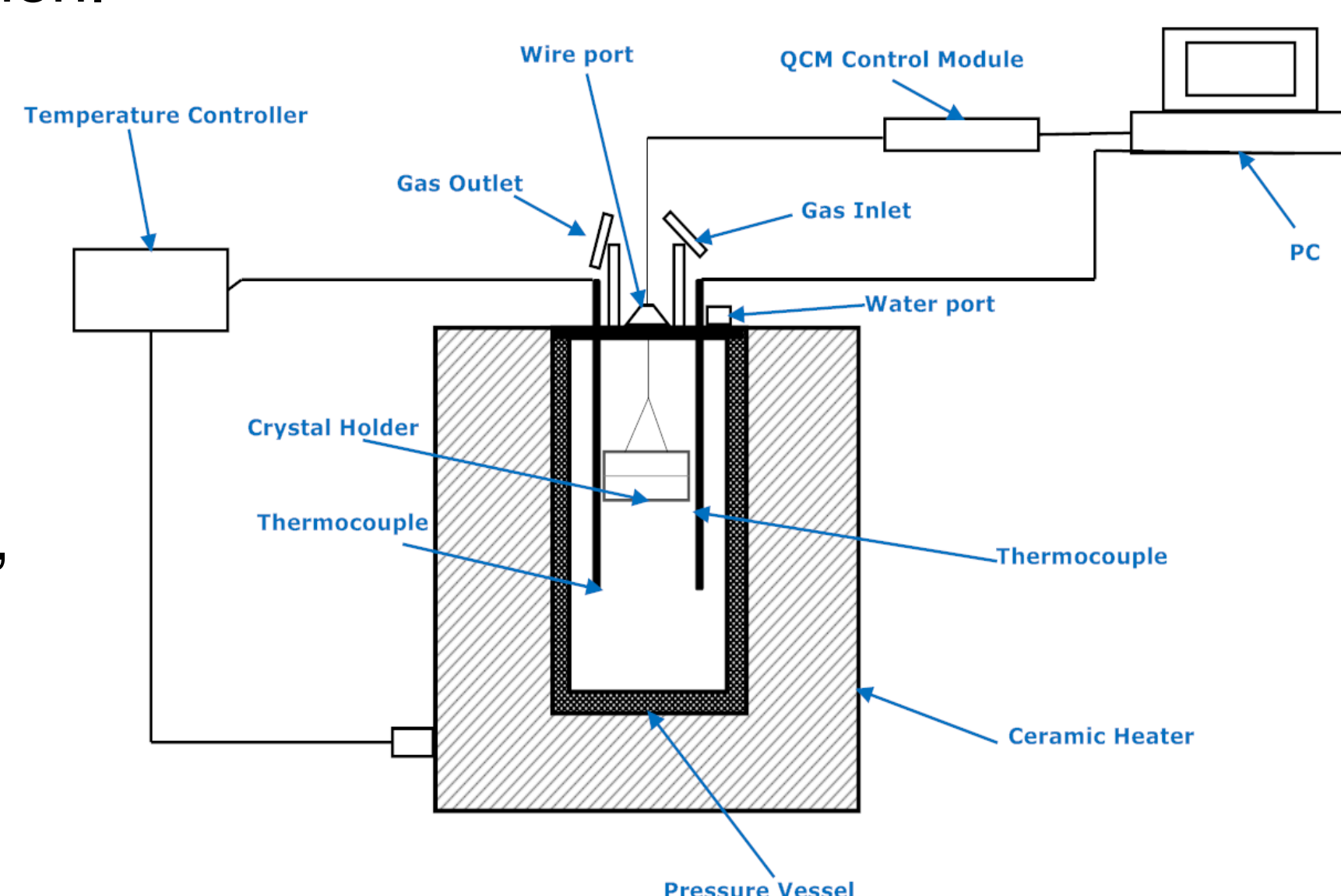


Fig. 1. Diagram of crystal microbalance experimental setup.

## Electrochemistry

Pure plutonium oxide is an insulator, limiting direct electro-chemical study. However, through doping with small amounts of other metals, the oxide can act a semi-conductor, allowing investigation of the thermodynamics of its redox chemistry. Through radioactive decay, aged plutonium oxide samples contain small amounts of americium and other metals. This will be mimicked through use of ceria or uranium oxide doped with europium.

## Conclusion and Further work

Initial studies have shown that absorption and desorption of water onto and from metal oxide layers can be measured using crystal microbalance methodology. The cubic frequency-temperature dependence of quartz crystals limit the use of this technique at higher temperatures. These studies are currently being repeated using GaPO<sub>4</sub> crystals that evince a quasi-linear temperature dependence.

Doped ceria and uranium oxide layers will also be produced by to allow electrochemical investigation of the oxide layers. This will give insight to any changes in metal oxidation state occureing, for example due to H<sub>2</sub> production.