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# An operando investigation on arsenic transformations under realistic bushfire conditions – the influence of organic matter and temperature

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Bushfires are increasing worldwide and are known to drive the cycling of nutrients and contaminants, including arsenic (As). Arsenic is a redox-sensitive metalloid which is sensitive to fire-driven processes. However, to date, only ex-situ experiments have been reported which primarily simulate extreme fire conditions. Little is currently known about As transformations during low-moderate bushfires. To investigate this, we used an operando X-ray absorption spectroscopy approach on tooeleite (a ferric As(III) bearing mineral) to examine real-time changes in As oxidation state in As-iron-organic matter systems under simulated low-moderate intensity (200-400°C, 0-120 min) bushfire conditions. For this experiment, tooeleite was mixed with humic acid at three levels (C/iron: 0, 2, and 10). During heating, rapid As K-edge XANES (X-ray absorption near edge spectroscopy) spectra were collected, complemented by *ex-situ* extended X-ray absorption fine structure spectroscopy (EXAFS). The XANES results show that without carbon (C/Fe=0), heating from 200-400°C promotes rapid redox changes, dominated by the transformation of As(III) to As(V), along with the formation of As(II). Approximately 60% As(III) was oxidised to As(V) within 60 min at 200°C. The As(V) state becomes dominant within 30 min upon heating at 300°C and reached ~85% by 120 min. At 400°C, changes occurred very quickly with 70% of As(III) oxidised to As(V) by 5 min and ~95% within 15 min.

Organic matter provided a protective effect on As transformation and decreased the rate of redox transformation. At C/Fe=2, As(III) started converting to As(V) after 30-40 min at 200°C, and at 300°C As(V) increasing from ~10-15% of total As at 10-15 min to ~65% by 120 min. Conversely, high organic matter (C/Fe=10) contents inhibited oxidation when heated at 200°C, and delayed oxidation at 300°C (almost 50% As(V) by 120 min). However, heating at 400°C with C/Fe=10 still allows substantial transformation of As(III) to As(V) within 30 min. Further, As K-edge and Fe K-edge EXAFS indicate that bushfire conditions promote crystallographic changes which enhanced As solubility. Our findings indicate that during bushfires, organic matter drives mixed redox states at low-moderate temperatures, but relatively higher intensity (>400°C) bushfires exceed this 'buffering capacity' and drive rapid arsenic transformation.