1. Fluorochemical Industry

Fluorochemicals are important molecules used in our everyday lives. For centuries, the first step in accessing all fluorochemicals has been the energy-intensive conversion of fluorspar (CaF$_2$) to highly toxic and corrosive hydrogen fluoride (HF) gas. A paradigm shift would be to access essential fluorochemicals directly from fluorspar bypassing HF, in a way that is cheaper, safer and greener. Our aim was to find a solution to this long-standing challenge.

2. Method: Mechanochemical Activation of CaF$_2$

1. CaF$_2$ is insoluble in water and all organic solvents. (e.g. ball milling) can be used to harness reactivity of insoluble salts.

2. Inspired by biomineralization (e.g. bone formation), where Ca$^{2+}$ ions form strong bonds with phosphate ions ($PO_4^{3-}$), we sought to replace fluoride (F$^-$) ions in CaF$_2$ for $PO_4^{2-}$ to release fluoride.

3. Grinding fluorspar (>97% CaF$_2$) with dipotassium phosphate (K$_2$HPO$_4$) in a ball mill enables F$^-$ release from CaF$_2$, increasing its solubility.

4. The resultant powder is a new, easy to handle fluorinating reagent (Fluromix™) that can be used to make fluorochemicals in a manner that completely bypasses HF production.

3. New Fluorinating Species

Powder X-ray diffraction was used to elucidate the composition of Fluromix™, which contains CaF$_2$ and 2 new crystalline salts X and Y.

X is K$_2$(HPO$_4$)$_2$F, independently prepared by ball milling $KF + K_2HPO_4$. Y is K$_2$Ca$_2$(PO$_4$)$_2$(PO$_4$)$_2$ prepared by ball milling X + CaHPO$_4$. Both X and Y possess fluorinating ability and are in Fluromix™.

4. Fluorochemicals from Fluromix™

Fluromix™ successfully installs F atoms into organic molecules by halogen exchange. It was used to synthesize a variety of fluorochemicals with S-F and C-F bonds including:

- Widely used fluorinating reagents
- Fluorochemicals used to make drugs and agrochemicals
- Industrially relevant chemical building blocks

Conclusions & Outlook

Mechanochemical activation of fluorspar (>97% CaF$_2$) with K$_2$HPO$_4$ affords a fluorinating reagent (Fluromix™) for the construction of S-F and C-F bonds without the requirement of HF. Complementary approaches to accessing fluorine content from waste fluorochemicals will form the focus of future work towards developing circular solutions to fluorine chemistry with global challenges in mind.