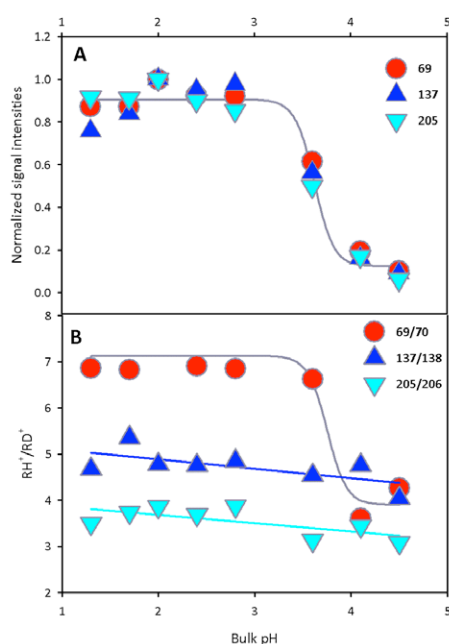


## Cationic polymerization of isoprene on cloudwater droplets

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We show that gas-phase isoprene is readily protonated and subsequently polymerized by collision with liquid microjets surface of mildly acidic water ( $1 < \text{pH} < 4$ ) within  $\sim 10$  ms. Kinetic isotope effects for the products formation were determined to reach up to 7, showing the direct evidence that the observed phenomena are due to a truly interfacial reactions initiated by proton on water. Since such reactions only occur at superacidic condition in homogeneous bulk media (e.g.,  $\text{pH} < -1$ ) or in pure gas phase, the surface of ambient atmospheric aerosol particles will behave as an unusual catalyst for reactive uptake of global gaseous unsaturated hydrocarbons.



**Figure 1:** A: Signals  $\text{IsoH}^+$  ( $m/z = 69$ ),  $(\text{Iso})_2\text{H}^+$  (137), and  $(\text{Iso})_3\text{H}^+$  (205) from protonation/polymerization of isoprene produced on  $\text{H}_2\text{O}:\text{D}_2\text{O}$  (50/50 = vol/vol) microjets exposed to 88 ppmv isoprene(g) for  $\sim 10$   $\mu\text{s}$  as a function of bulk pH. B: Kinetic isotope effects (KIE) for the products of isoprene (g) on  $\text{H}_2\text{O}:\text{D}_2\text{O}$  (50/50 = vol/vol) microjets exposed to 88 ppmv isoprene (g) as a function of bulk pH. All experiments in 1 atm  $\text{N}_2(\text{g})$  at 293 K.

## Testing the use of detrital rutile to investigate HP/UHP rocks

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Accessory rutile generally is the main host of Ti in HP/UHP metamorphic rocks. It is also a major carrier of HFSE, providing a potential tracer of contrasting tectonic processes. For example, the Zr-in-rutile geothermometer has now been widely and successfully applied to HP rocks, and Cr/Nb ratios have been used to distinguish between different bulk composition of the host rock. Moreover, rutile is a robust mineral in sedimentary environments and is common as an accessory phase in sandstones. Therefore, its potential as a detrital tracer of HP metamorphism is high. Metamafic and metapelitic rocks from two case studies located in Syros, Greece and the Western Alps, both settings displaying HP/UHP conditions, have been sampled together with sediments that resulted from the erosion of these rocks in beach and river catchments. The geochemical correlation of rutile between source rocks and sediments is assessed based on its HFSE budget.

This study aims to establish geochemical signatures of rutile that are characteristic for detrital grains sourced from HP/UHP rocks formed in subduction zones. The Zr-in-rutile thermometer [1, 2] provides peak metamorphic temperatures for the investigated samples that are coherent with published peak temperatures for the respective metamorphic sequences. In addition, the calculated temperatures are independent of the source rock lithologies, i.e., the presence or absence of quartz. The T histograms for the Western Alps indicate a low-T peak, suggesting the blueschists, eclogites and Dora Maira rocks are dominant, and not the high-T Ivrea rocks, as expected. Cr/Nb ratios have been employed successfully and *in situ* analysis fall strictly into the mafic (for Syros) and pelitic (for the Western Alps) source rock fields [3, 4, 5].

[1] Zack *et al* (2004b) *CMP* **148**, 471–488. [2] Watson *et al* (2006) *CMP* **151**, 413–433. [3] Zack *et al* (2002) *Chem. Geo.*, **184**, 97–122. [4] Zack *et al.* (2004a), *Sed. Geo.*, **171**, 37–58. [5] Meinhold (2010) *E-S Rev.* **102**, 1–28.