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Measuring the Activation Energy of Cartilage

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WELMEC, University of Leeds

**Medical Engineering Centres Annual Meeting and
Bioengineering14**

Imperial College London, 10-11 September 2014



- Investigate if NMR parameters could be used to extract structural, functional and physical information through imaging techniques
- To investigate different methods of generating contrast within cartilage using MRI
- Learn about the local environment of the cartilage by using the water/fluid within it as a probe.



- Simple model for relating reaction rate to temperature

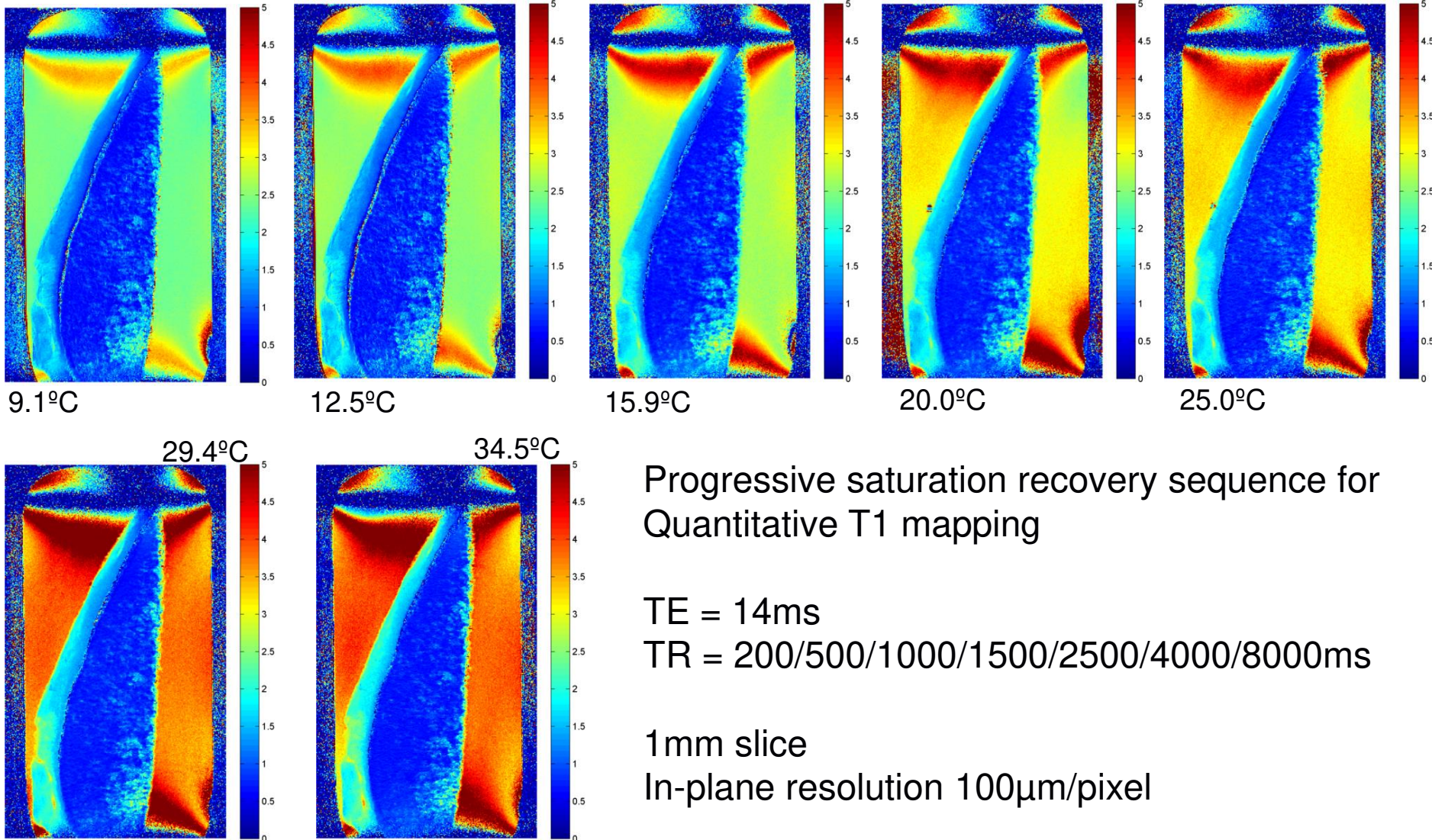
$$k = A \exp\left(-\frac{E_A}{RT}\right)$$

- Can be used as a probe to determine sensitivity of a parameter to temperature
- T1 or Spin-lattice relaxation time is describes the rate at which the longitudinal magnetisation in a sample recovers towards thermal equilibrium
- Although there are many factors that contribute to T1 relaxation – rotation dynamics dominate to a good first approximation

Relaxation Time Mapping



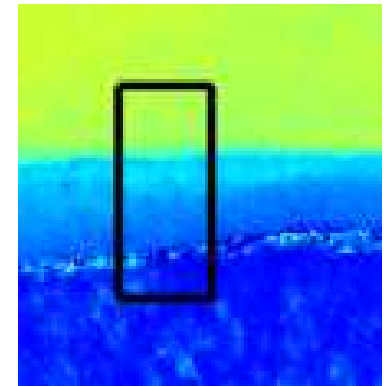
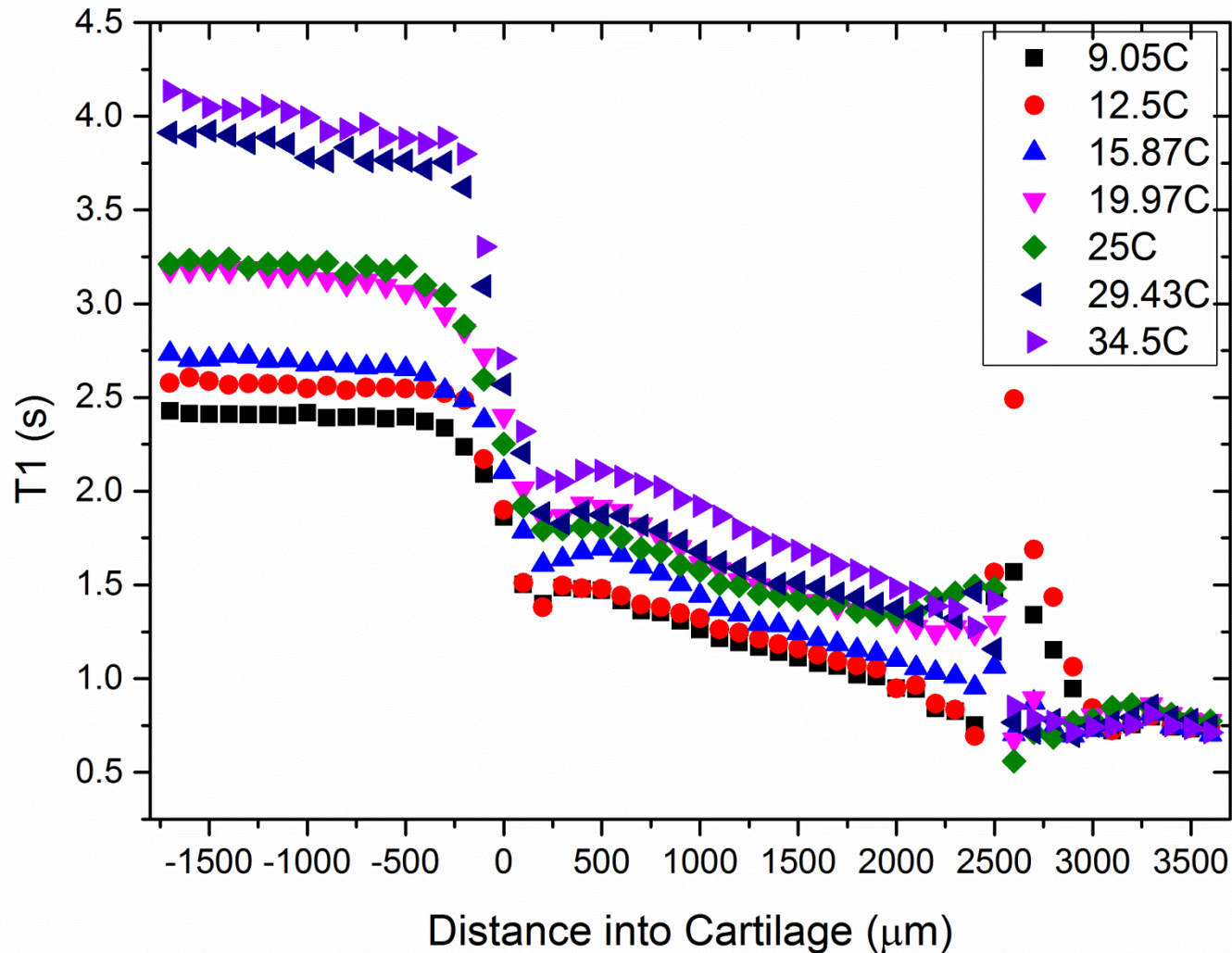
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T1 profiles



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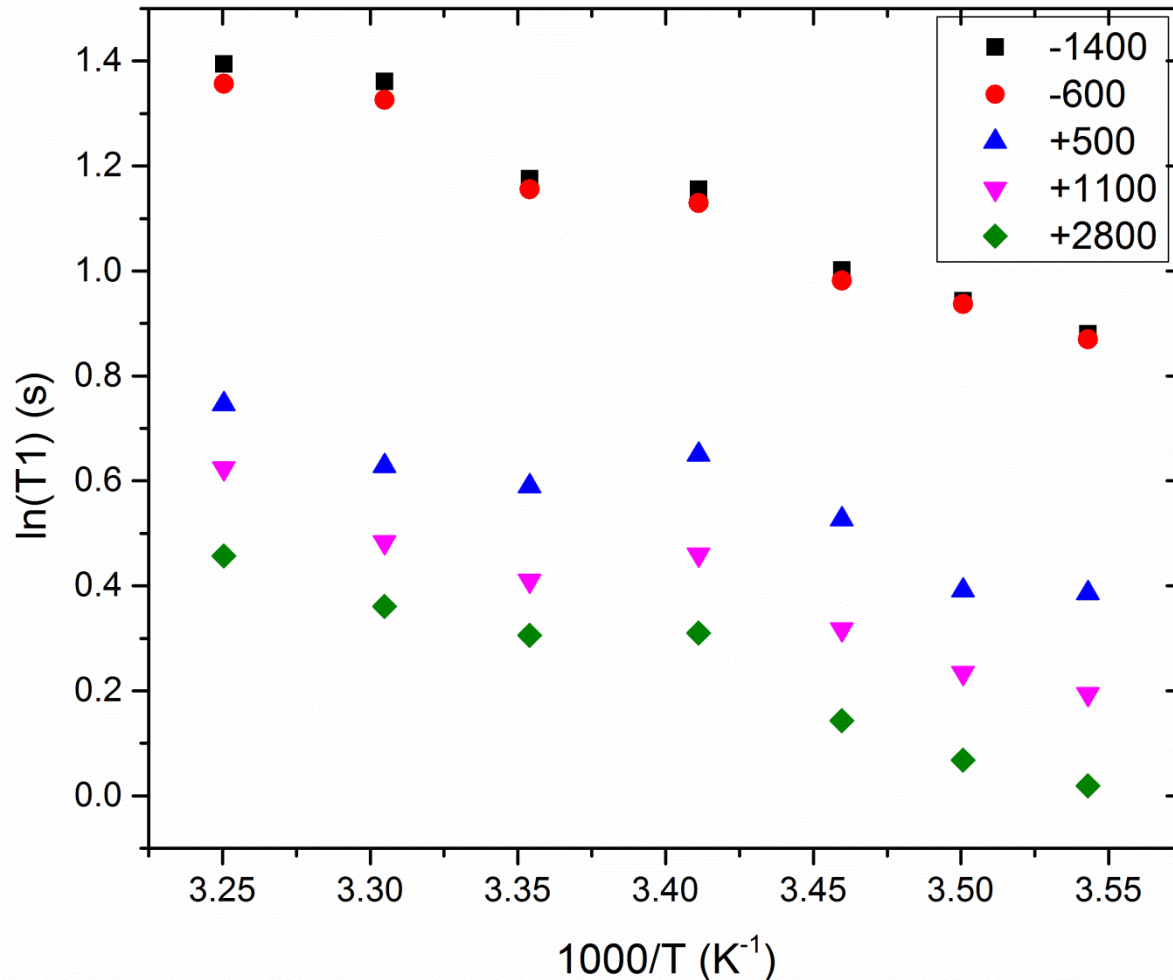
Human Cartilage

Average T1
across each row
as function of
Temperature

Arrhenius Relationship



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Arrhenius relationship

$$\frac{1}{T_1} \propto \exp\left(\frac{-E_A}{RT}\right)$$

Data is linear

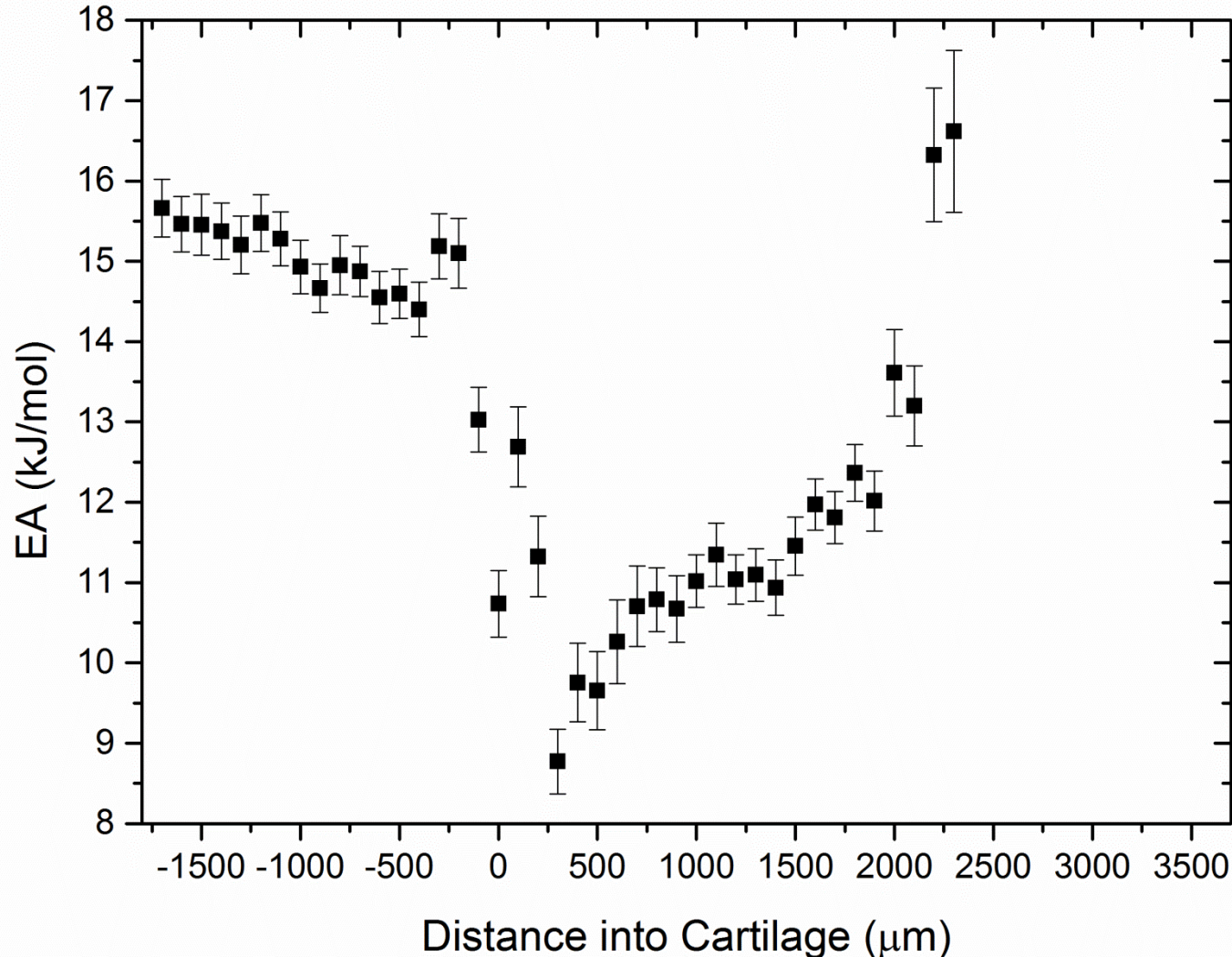
Activation energy
given by gradient

2 pixels in PBS
1 pixel near surface of
cartilage (blue)
1 middle (pink)
1 deeper (green)

T1 Activation Energy Profiles



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T1 EA shows variation with depth

EA value in cartilage lower than that of PBS/water

EA gradually increases with depth (as opposed to T1, which decreases)

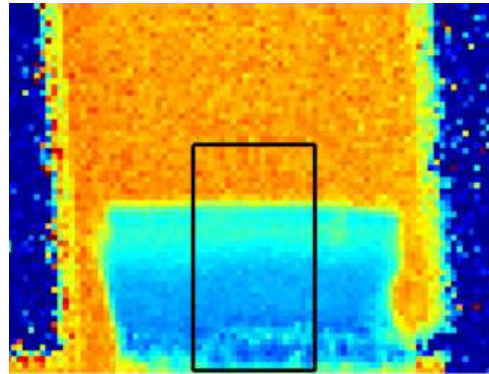
EA of pure water 16.6kJ/mol

Simpson & Carr
Phys Rev 111 (1958) v5 1201

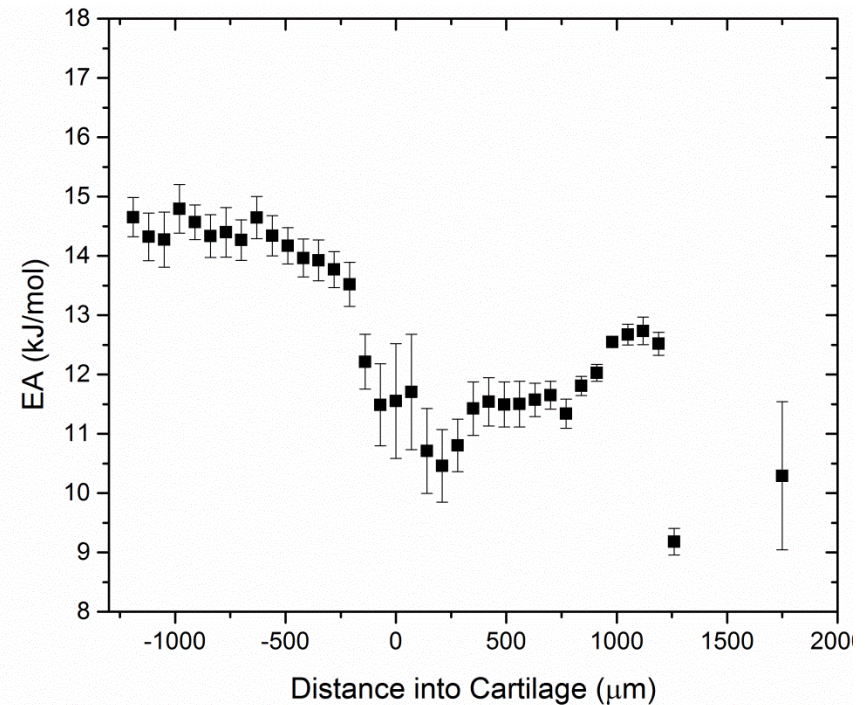
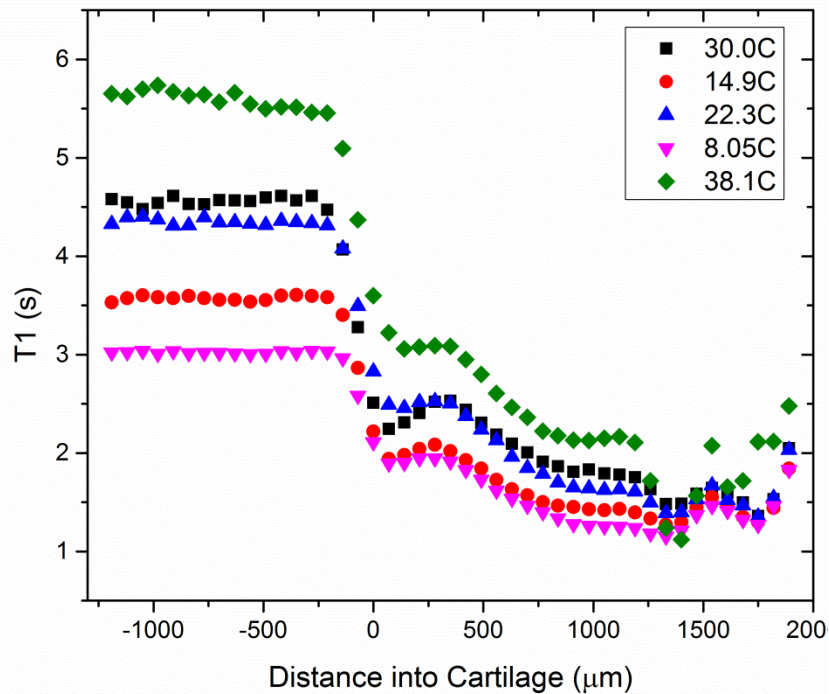
Bovine Cartilage



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Bovine cartilage exhibits similar behaviour



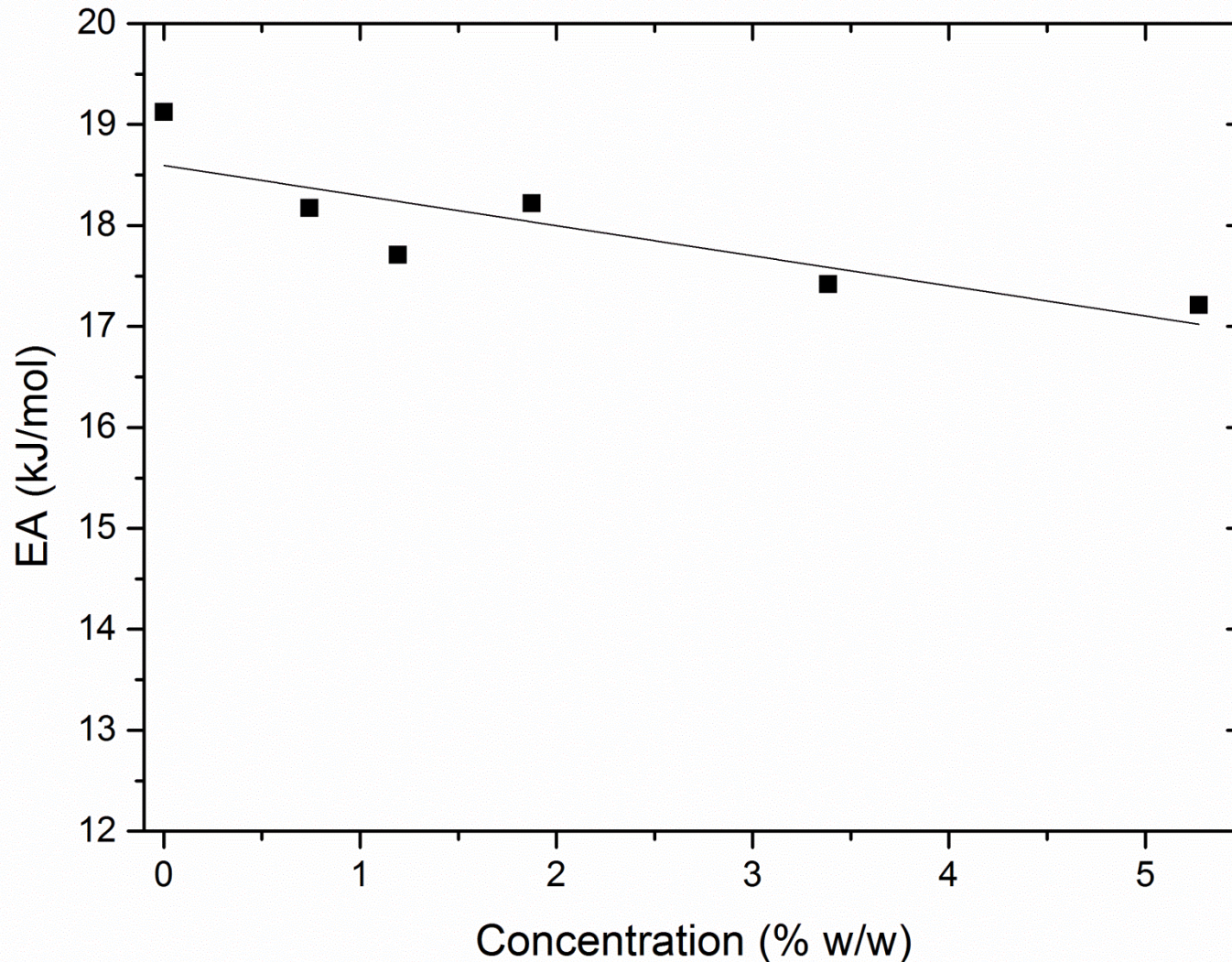


- Aim: look at the microscopic origins of EA – investigate GAG concentrations as a function of temperature
- Range of solutions of aggrecan EA in solution from 0.7% to 5.3% w/w
- T1 NMR (i.e. non-imaging) at a range of temperatures 8°C to 38°C
- EA calculated from measured relaxation rates

GAG activation energy



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T1 EA in Aggrecan samples show little variation in EA with concentration

Suggests EA flavour in cartilage must be due to other constituents



- Activation Energy from quantitative T1 mapping changes with depth through cartilage
- The EA through the main bulk of the cartilage is lower than that in water (PBS)
- Loss in 'structure' of the water molecules through the cartilage matrix due to confinement lowers EA
- We suggest that in the deeper parts of the cartilage, EA increases due to increased binding
- No variation in EA from T1 with Aggrecan concentration – other constituents influencing EA

Acknowledgements



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