

Why you Can't Use Water to Make Cryoporometric Measurements of the Pore Size Distributions in Meteorites – or in High Iron Content Clays, Rocks or Concrete.

J. Beau W. Webber^{a,c,d}, *Philip Bland*^b, *John H. Strange*^c, *Ross Anderson*^a, *Bahman Tohidi*^a

^aInstitute of Petroleum Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, UK;

^bImperial College London, South Kensington Campus, London SW7 2AZ, UK;

^cSchool of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NH, UK;

Corresponding author: J. Beau W. Webber, Lab-Tools Ltd., G19 Canterbury Enterprise Hub, University of Kent, CT2 7NJ, UK. E-Mail: J.B.W.Webber@kent.ac.uk

(received 11 July 2008, accepted 15 October 2008)

Abstract

Many porous materials have high susceptibility magnetic gradients in the pores, due to the presence of iron or other magnetic materials. Thus if probe liquids are placed in the pores they exhibit fast decaying signals with a short T_2^* . Usually the actual T_2 of the liquids is also reduced, due the presence of paramagnetic ions in the pore walls. The usual solution in NMR is to measure an echo (or echo train) at short times. However, recent work [J. Phys.: Condens. Matter 19, 415117, 2007.] has shown that water/ice systems near a pore wall form rotator phase plastic ice, with T_2 relaxation times in the region of 100 to 200 ms. Thus if a NMR cryoporometric measurement is attempted with a measurement time significantly less than 1 or 2 milli-seconds, the result is to make a measurement based on the phase properties of the brittle to plastic ice phase transition, not that of the brittle ice to water phase transition. This gives rise to artefacts of small pore sizes that may not actually be present. This work successfully uses a-polar liquids instead.

Keywords

confined geometry, plastic ice, cryoporometry, meteorite, porosity.

1. INTRODUCTION

Many porous materials have high susceptibility magnetic gradients in the pores, due to the presence of iron or other magnetic materials. Thus if probe liquids are placed in the pores they exhibit fast decaying signals with a short T_2^* . The actual T_2 of the liquids is also reduced, due the presence of paramagnetic ions in the pore walls. The usual solution in NMR is to measure an echo (or echo train) at short times. However water/ice systems near a pore wall form rotator phase plastic ice^[1], with T_2 relaxation times in the region of 100 to 200 ms (Fig. 2).

Thus if a NMR cryoporometric measurement is attempted with a measurement time significantly less than 1 or 2 ms, the result is to make a measurement based on the phase properties of the brittle to plastic ice phase transition, not that of the brittle ice to water phase transition (Fig.2.). If the assumption is made that one is measuring the usual transition to the liquid phase, this gives rise to artifacts of small pore sizes that may not actually be present in the sample. A solution to this problem is presented.

1.1. Aqueous alteration in asteroids :

High porosity \neq high permeability

Carbonaceous chondrite meteorites are amongst the most chemically primitive objects in the solar system, yet many have experienced extensive aqueous alteration, apparently within asteroid parent bodies^[2]. Unfractionated soluble elements suggest minimal flow of liquid water, consistent with data from oxygen isotopes and meteorite petrography. However, numerical studies have persistently shown large-scale water transport in model asteroids. Vesicles, voids and inclusions can be seen in depth in this stereo view.

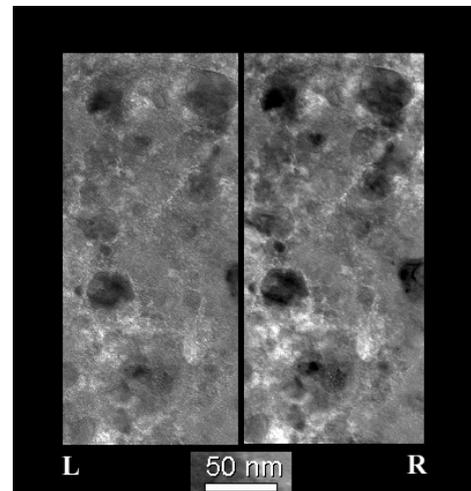


Fig. 1. Meteorite Acfer 094. Stereo TEM Micrograph.

2. NMR cryoporometry

This technique probes changes in the Gibbs free-energy by measuring changes in the freezing and melting transitions^[3]. In a pore the melting and freezing point of a liquid are depressed by an amount proportional to the inverse of the pore diameter x :

$$\Delta T_m = T_m - T_m(x) \approx \frac{a_p}{v_p} \cdot \frac{\sigma_{sl} T_m \cos(\phi)}{\Delta H_f \rho_s} \approx \frac{k_d \sigma_{sl} T_m}{x \Delta H_f \rho_s}$$

2.1 Brittle-Plastic Phase Transitions - in water/ice systems in SBA-15 porous silica.

NMR relaxation measurements, combined with neutron scattering data, indicate that there is an equilibrium state within the interfacial layer in the pores, such that, below the melting point, the ice changes continuously and reversibly with temperature between a brittle (mainly cubic) crystalline phase and a plastic disordered rotator phase.

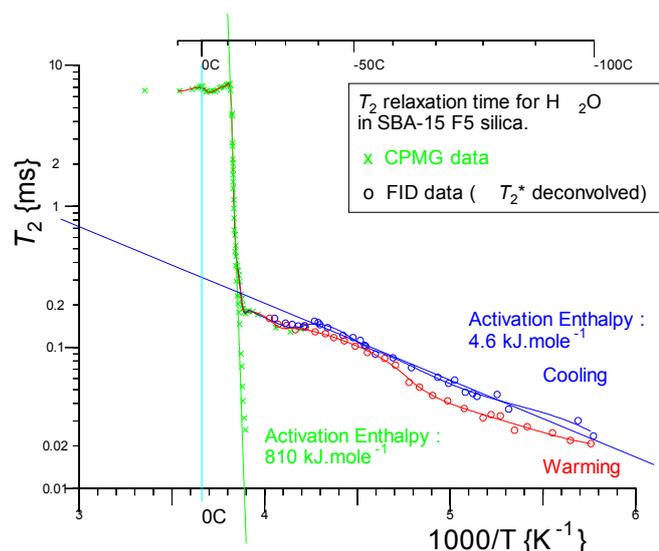


Fig 2. NMR relaxation rates T_2 for plastic ice in SBA-15 silica pores.

3. NMR on Meteorites.

Many meteorites are highly metallic and even magnetic, giving rise to huge magnetic gradients when placed in the normally uniform B_0 field of an NMR magnet. Thus there is a need to measure the signal from an echo at short times 2τ . This effectively then accesses the

brittle ice to plastic phase transition, not the brittle ice to liquid phase transition. Fig. 3 shows an NMR echo sequence in an ALH77307 meteorite sample, using an a-polar liquid; Fig. 4 shows corresponding cryoporometric curves successfully measured from such echoes.

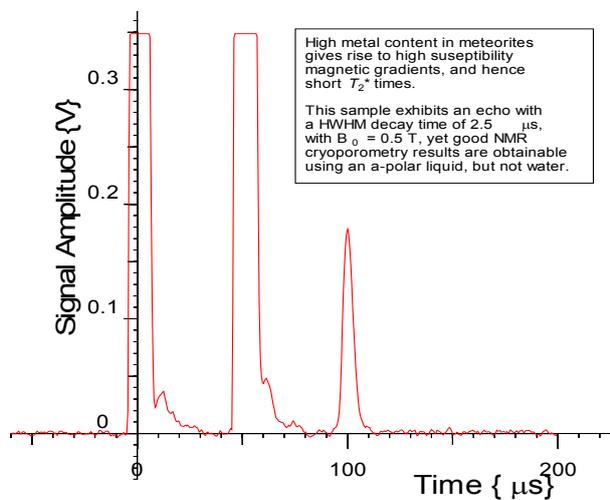


Fig. 3: NMR Spin-Echo from an a-polar liquid in a Meteorite sample ALH77307. Due to susceptibility gradients, the echo has a decay time HWHM of 2.5 μs

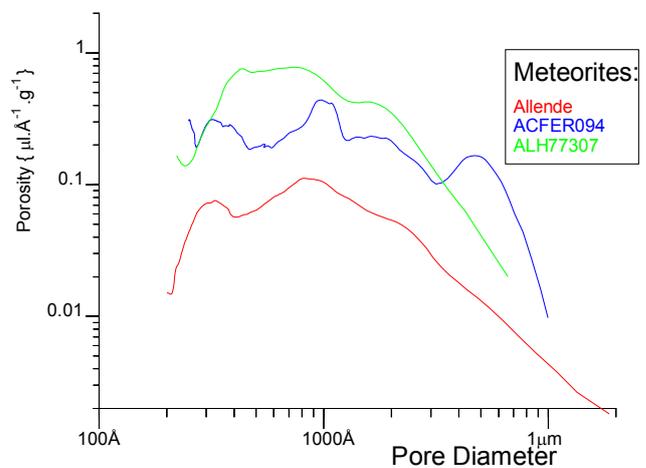


Fig. 4: Pore size distributions for 3 Meteorite samples, as measured by NMR cryoporometry, using an a-polar liquid.

4. Conclusions

NMR cryoporometry has been successfully performed using an a-polar liquid, avoiding the longish T_2 of plastic ice when using water. The T_2 of the frozen a-polar liquid is extended compared with that of the bulk value, suggesting that rotational motion may be present, but it is not as long as in the case of ice, such that the magnetization in the frozen component has substantially decayed by the echo time.

Preliminary NMR cryoporometry measurements of pore-size distributions in meteorites, using an a-polar liquid, successfully shows that the high porosity in meteorites extends over a wide range of pore diameters, down to small pore sizes.

The large number of small pores has restricted the ability of liquids to flow freely in the original asteroidal material.

References

- [1] Plastic ice in confined geometry: The evidence from neutron diffraction and NMR relaxation. J. Beau W. Webber, John C Dore, John H. Strange, Ross Anderson, Bahman Tohidi. *J. Phys.: Condens. Matter* 19, 415117, 2007, Special Issue: Proceedings of The International Workshop On Current Challenges in Liquid and Glass Science (The Cosener's House, Abingdon, UK, 10-12 January 2007).
- [2] Volatile fractionation in the early Solar System and chondrule/matrix complementarity. Bland, P. A., Alard, O., Benedix, G. K., Kearsley, A. T., Menzies, O. N., Watt, L. & Rogers, N. W. *Proc. Natl Acad. Sci. USA* 102, 13755-13760 (2005).
- [3] Nuclear Magnetic Resonance Cryoporometry J. Mitchell, J. Beau W. Webber and J.H. Strange. *Physics Reports*, 461, 1-36, 2008. doi:10.1016/j.physrep.2008.02.001