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Magnetic water treatment – how might it work?†

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Claims that passing hard water through a magnetic field somehow influences the structure and morphology of the calcium carbonate that forms when the water is subsequently heated have been met with robust scepticism. This was largely due to the absence of any plausible mechanism whereby water could acquire a long-lasting magnetically-imprinted memory. Recent work challenging classical nucleation theory, insofar as calcium carbonate is concerned, has advanced the idea of liquid-like prenucleation clusters of indeterminate shape that are thermodynamically-stable in calcium carbonate solutions. These nanometer-scale clusters may be the key to the problem; the possible influence on them of a magnetic field via Maxwell-like stress or singlet–triplet mixing of proton dimers leading to a long-lived change in the number of ionic bonds is discussed.

Keywords: magnetic water treatment; calcium carbonate; nucleation; magnetic properties; crystal growth

Reports of magnetic water treatment to modify subsequent limescale formation had been dismissed or ignored by the scientific community because there was no credible mechanism to explain how it could work. This article seizes on recent evidence of a non-classical nucleation mechanism for CaCO_3 , via prenucleation clusters which exist in equilibrium under ambient conditions, to suggest that a long-lived chemical memory could be imprinted on these clusters as they pass through the magnetic treatment device.

Magnetic water treatment is a scientific backwater. Researchers who venture there encounter a whiff of charlatanry alongside the sweat of baffled, evidence-based rational enquiry. Laying aside some of the more bizarre claims for ‘magnetic water’ (stronger concrete, improved crops, healthier or better-tasting tea), a basic proposition that is amenable to investigation is the following: By passing hard water through a magnetic field, typically generated by a patented configuration of permanent magnets, it is possible to influence the subsequent formation of limescale when the water is heated and becomes supersaturated in calcium carbonate [1]. Specifically, the costly problem of hard limescale forming on the inside surfaces of pipes, boilers, heat exchangers and even electric kettles is ameliorated, or even reversed. The early literature on the subject was reviewed by Baker and Judd [2].

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†Dedicated to David Sherrington, on the occasion of his 70th birthday.

Calcium carbonate, CaCO_3 , is unusual in that it is polymorphic; there are three crystalline varieties, two hydrates and several amorphous forms. Some information about the three crystalline polymorphs in order of decreasing stability, calcite, aragonite and vaterite, is collected in Table 1. Calcite and aragonite are both common rock-forming minerals. Calcite and vaterite are polar, but aragonite is not. Calcium carbonate is also unusual in that its solubility in water decreases with increasing temperature, which is why limescale forms when the water is heated.

Several independent investigations [3–6] have established that magnetic treatment influences the size and morphology of the calcium carbonate crystallites that form, with a tendency to favour the crystallization of aragonite rather than calcite, although it depends as well on the substrate and the composition of the water [7]. This might explain the efficacy claimed for the treatment, because the calcite builds up into hard scale, whereas the aragonite in these studies forms a slushy precipitate, which is easily washed away. The data include a series of blind tests where the hypothesis that the treatment has *no* effect on the calcite/aragonite ratio was dismissed at almost the 4σ confidence level [4]. Furthermore, tests with controls on domestic hot water tanks [8] and industrial-scale heat exchangers [9,10] support the notion that magnetic water treatment works. What is not explained, and seems to verge on the miraculous, is that it is possible to influence the carbonate precipitation process by magnetic treatment of the water that took place minutes or even hours beforehand.

Provided there is no inadvertent chemical contamination [11,12], which is easy enough to avoid if the magnets creating the field are external to the vessel containing the water, there seem to be just two possibilities – the passage through the magnetic field has altered either:

- (a) the structure or chemical composition of the water itself, or
- (b) the structure of the dissolved calcium carbonate.

Both appear fanciful. Memory effects in water have an unhappy history, going back to the polywater fiasco [13]. Classical nucleation depends on stochastic fluctuations in the local concentration of dissolved ions to form a tiny crystalline seed, which has a slight chance of growing into a crystallite in appropriate conditions of supersaturation [14]. The magnetic treatment is performed on undersaturated solution, and the time between treatment and precipitation can exceed the lifetime of a classical nucleus by nine or more orders of magnitude. For want of a plausible explanation, the scientific community has tended to view reports of magnetic water

Table 1. Properties of crystalline polymorphs of CaCO_3 .

Phase	Point group	Space group	Lattice parameters (nm)	Density (kg m^{-3})
Calcite	$3m$	$R3c$	$a = 0.499, c = 1.706$	2701
Aragonite	222	$Pmcn$	$a = 0.496, b = 0.797, c = 0.574$	2940
Vaterite	$6mm$	$P6_3/mmc$	$a = 0.714, c = 1.698$	2560

treatment with embarrassment, or disregard them altogether. There is a refreshingly sceptical website devoted to the topic [15], and it has been advocated as a means to initiate students to the mysteries of Nature as well as the joys of evidence-based enquiry [16].

Here we reconsider the problem in the light of recent reports by Gebauer et al. [17] and Pouget et al. [18] that challenge classical nucleation theory [14]; they suggest that thermodynamically-stable prenucleation clusters exist in undersaturated CaCO_3 solutions. These clusters and the associated nonclassical nucleation are discussed by Raiteri and Gale [19] and reviewed by Gebauer and Cölfen [20]. Evidence comes from measurements of the free calcium in solution, ultracentrifuge experiments, cryo-TEM and mass spectroscopy [18–21] that the prenuclei are clusters of several tens of atoms, about a nanometer in size, which exist in equilibrium in aqueous calcium carbonate solutions. The structure of these stable prenuclei has not yet been determined experimentally, but the ions in them remain hydrated [19], and they can account for as much as half the calcium present in solution [18]. Molecular dynamics simulations show the clusters are disordered, hydrated flexible ionic polymers [22], with no preferred shape. Their radius of gyration may change by a factor of two at an energy cost that is less than the thermal energy, $k_B T$. These sloppy objects have earned the felicitous name of DOLLOPs (dynamically-ordered liquid-like oxyanion polymers) [22]. The hydrated multinuclear carbonate complexes of calcium and other divalent cations are found to aggregate into much larger (4–100 nm) particles [18–21], forming a liquid emulsion at neutral pH [21]. Different prenucleation clusters have been implicated in the crystallization of calcite and vaterite from different amorphous calcium carbonate (ACC) precursors [23]; the chemical composition of the water can also influence the ACC and the crystallization outcome [24]. Since these prenucleation clusters and their aggregates are supposed to exist in equilibrium in water, they may help to explain the long-lived memory effect, provided the magnetic treatment is capable of favouring one type of cluster over another, and the relaxation time for changes in the relative population of the two is very long. The role of the magnetic field is now to leave a long-lived imprint on the DOLLOPs, not on the water itself.

Next, we speculate on how short exposure to a magnetic field might possibly modify these clusters in a way that can lead to the preferred crystallization of one or other of the calcium carbonate polymorphs.

The force on an ionic charge q moving with velocity \mathbf{v} through a region where there is an electric field \mathbf{E} and a magnetic field \mathbf{B} is given by the Lorentz expression

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (1)$$

In magnetic water treatment devices, the velocity of the water and the magnetic field rarely exceed 0.1 ms^{-1} and 1 T, respectively. The equivalent electric field $\mathbf{E}' = \mathbf{v} \times \mathbf{B}$ will be less than 100 mV m^{-1} . Even allowing for a high dielectric constant, the induced electric dipole moment will be pitifully small (Figure 1a).

However, if the prenucleation clusters are charged in such a way that the electric dipole moment is pre-existing, rather than induced by motion through the field, there is stress on the cluster as it passes through. Imagine that opposite faces of the cluster are oppositely charged (Figure 1b), and the separation of the charges ne on the

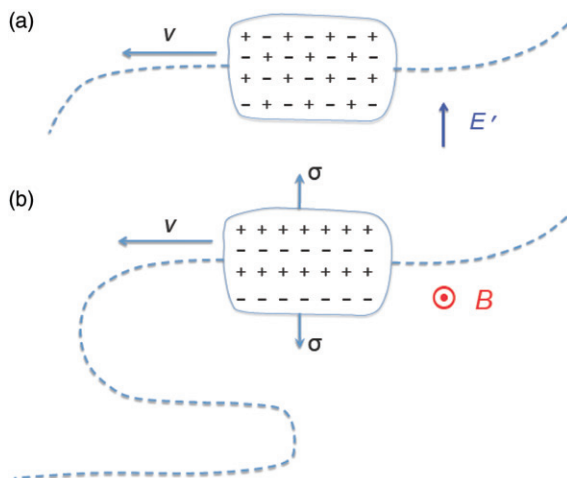


Figure 1. Schematic illustration of a prenucleation cluster, comparing nonpolar (a) and polar (b) structures. The nonpolar cluster is subject to a weak electric field E' as it moves through the magnetic field, but the polar cluster is subject to a stress σ , which is independent of the direction of motion.

surface is a , the stress on the particle is then approximately

$$\sigma = nevB/a^2, \quad (2)$$

independent of particle size. Taking $n=2$ and $a=0.25$ nm, we find that the magnitude of σ is about 0.5 N m^{-2} . This is not a large stress, although it should not be forgotten that a DOLLOP is a shapeless, liquid-like blob that is easily deformed. Maxwell stresses less than an order of magnitude greater are capable of severely deforming the shape of small (<1 mm) tubes of paramagnetic ionic solutions in water [25].

It is therefore not entirely fanciful to imagine that the DOLLOPS, or aggregates of them, could be significantly deformed during their passage through the magnetic field. The dwell time of the water in the magnetic device is of order 100 ms. The effect of the field will first be to exert a torque on the charged particle, which will tend to align it with the flow (Figure 1a). The time τ involved will be of order

$$\tau = \rho\nu/\sigma, \quad (3)$$

where ν is the kinematic viscosity ($\approx 10^{-6} \text{ m}^2 \text{ s}^{-1}$) and ρ is the density of the electrolyte. The time τ is of order milliseconds, and it is independent of the radius of the prenucleation cluster because both the stress and the viscous force scale with the surface area of the particle. The stress can be expected to act as long as the prenucleus is moving in the magnetic field. Turbulence is beneficial, because the fluid velocity will be greater in eddies, and even if the flow direction is reversed, the stress continues to act in the same sense (Figure 1b). We would like the deformation of the prenuclei aggregates by stress to be sufficient to somehow change them from quasi-stable proto-calcite to quasi-stable proto-aragonite, or otherwise modify their

colloidal properties and the subsequent crystallization pathway. The size l of a DOLLOP that would experience a deformation energy of order $k_B T$ is given by

$$\sigma l^3 > k_B T, \quad (4)$$

which means that l should be greater than about 200 nm. This is much larger than the observed size of the prenucleation clusters, and it is an underestimate. Hour-long stability against thermal fluctuations requires an energy barrier between the two states of about $30 k_B T$.

The polar character of the prenucleation clusters might be expected to influence that of the crystallites that grow from them. Of the CaCO_3 polymorphs, calcite and vaterite are polar (pyroelectric), so the anticipated effect of the magnetic treatment may be to convert polar (calcite) prenuclei into nonpolar (aragonite) ones. Unfortunately, it appears that purely mechanical stress will be unable to induce changes in the structure and branching in objects as small as the DOLLOPs which would resist thermal erasure on the required timescale. A magnetically-induced modification with much longer staying power is required.

A clue may be found in the papers of Lundager Madsen on the influence of a magnetic field applied *in situ* on the growth from solution of crystals of sparingly-soluble ionic solids such as calcium carbonate [26–28]. Effects are found for carbonates and phosphates of Mg, Cd and Zn, but not of Mn, Fe or Co. Furthermore, the effects are absent at high pH, or when heavy water (D_2O) is used as the solvent. He concludes that the crystallizing salt must be diamagnetic (or only weakly paramagnetic), the anion must be a strong base and that proton transfer and quantum statistics play a key role.

At this point it is worth recalling that the nuclear isomers of dihydrogen can be remarkably long-lived. Ortho-hydrogen and para-hydrogen are the textbook example [29], with total nuclear spins $I=1$ and $I=0$, respectively. The two species, with parallel and antiparallel nuclear spins, have an equilibrium concentration ratio of 3:1, but ortho–para interconversion is constrained by the need to conserve angular momentum, which means that it often involves a rotational excited state. Para-hydrogen with no net angular momentum lies 175 K lower in energy than the lowest rotational state of ortho-hydrogen. Interconversion in the gas phase can be so slow that the two nuclear isomers may be regarded as separable species, with distinct physical properties. Nonequilibrium concentration ratios of the two species can persist in the gas phase for hours or even days.

Likewise, water exists in two nuclear isomers, but the energy separation is only 34 K. They were recently separated in a molecular beam using a Stern-Gerlach apparatus [30]. There are also claims that ortho- and para-water can be separated by absorption in a chromatography column [31], or at the surface of glycerol [32], and that their lifetime in ice is at least a few months. Remarkably, the isomers were claimed to be long-lived in the liquid state, where the lifetime of para-water ($I=0$) was found to be 26 min whereas that of ortho-water ($I=1$) was 55 min [31]. More recently, the isomeric separation by absorption has been questioned [33], and it is thought that proton exchange should limit the lifetime of the isomers of water in the liquid state to milliseconds or less [34,35].

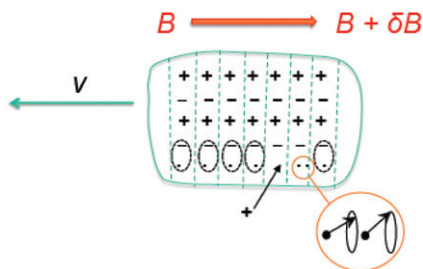


Figure 2. Schematic illustration of a small aggregate of prenucleation clusters, which are short chains of Ca^{2+} and CO_3^{2-} ions, represented by + and - signs, respectively, surrounded by water. The HCO_3^- ions at the negatively-charged surface are indicated by dashed ovals. Addition of a Ca^{2+} ion at the surface is facilitated by the magnetic field gradient, which causes dephasing of the spins of a proton dimer as they precess at different rates in the inhomogeneous field.

If the magnetic treatment does not exert a long-lived influence on the water itself, the alternative is to look for an effect on the prenucleation clusters. We need a mechanism whereby passage through an inhomogeneous magnetic field can effect a lasting change in their chemical structure. In Figure 2, we show a schematic image of a small aggregate of clusters which has positively-charged Ca^{2+} ions on one face and HCO_3^- anions on the other. (Bicarbonate is the predominant carbonate species in solution at neutral pH). The water is not shown. If the prenucleus is to grow, the proton shield must be removed to allow addition of the next layer of Ca^{2+} ions. When a Ca^{2+} ion is added to the HCO_3^- surface in Figure 2, it has to displace a proton which can lead to the fleeting formation of a hydrogen dimer in H_2CO_3 or in its stable product $\text{H}_2\text{O} + \text{CO}_2$.

Dimerization of the protons in the prenucleation cluster seems to be a necessary condition for long-lived modification of the clusters by passing them through an inhomogeneous magnetic field, which has the effect of scrambling the proton singlets and triplets. The proton spins will precess in a field B at the Larmor frequency $f_p B$, where $f_p = 42.6 \text{ MHz T}^{-1}$. If the spins in a dimer with separation a are to be dephased in the course of their passage through the magnetic device, they must precess at slightly different frequencies so that the accumulated phase difference is π or more. The condition for an appreciable magnetic field effect is

$$C = 2(L/v)f_p a \nabla B \geq 1. \quad (5)$$

If we suppose that the DOLLOPs move with velocity v through the magnetic device of length L which produces a magnetic field gradient ∇B , and take representative values $L = 5 \text{ cm}$, $v = 0.1 \text{ ms}^{-1}$, we find that a field gradient of order 100 T m^{-1} is needed. Many magnetic water treatment devices use permanent magnet arrays to generate field gradients of this magnitude. It should therefore be possible to modify the relative populations of the singlet and triplet proton dimers in these devices. This, in turn, should alter the nature of the prenucleation cluster, whether by reaction with ionic species within the device itself, or subsequently. From our reading of the literature, it appears unlikely that nonequilibrium singlet:triplet ratios can survive for many hours in an aqueous environment, so we will consider how a long-

lived modification of the prenucleation cluster could be effected within the magnetic treatment device, or just downstream of it.

The addition of an extra calcium ion in Figure 2 increases the length of one of the prenucleation cluster chains in the aggregate; it requires displacement of a proton to an adjacent site, where H_2CO_3 or H_2O may be formed. Transfer of a proton to an adjacent HCO_3^- ion involves an activation barrier, which was found in molecular dynamics simulations to be 18 kJ mol^{-1} [36], but this may be much reduced by the coulomb interaction with the added calcium ion. The barrier will also depend on the nuclear spin, with the nuclear triplet p -like state lying higher in energy than the nuclear singlet s -like state by an energy roughly of order $(3/4)Z^2$ times the ‘proton Rydberg’ $m_p e^4 / 8\epsilon_0 h^2$ with $Z=2$ (258 K). The coulomb interaction will be screened by the polarizability of the oxygen anion, and it will certainly be modified at the surface of the prenucleation cluster. The idea is that in the absence of a magnetic field, the triplets are unstable and do not form H_2CO_3 or H_2O . In the nonuniform field, however, the triplets will dephase and convert to the more strongly-bound singlets, increasing the chances of calcium addition.

Furthermore, there is evidence that the nuclear singlet is spin protected, in the sense that its lifetime can exceed the proton spin-lattice relaxation time by an order of magnitude or more [37]; the lifetime could certainly be comparable to the time spent by the prenucleation cluster in the magnetic device. After taking on board an extra Ca^{2+} ion, the new cluster may be stable for a long time, since the energy of the ionic bond formed is of order $0.1 u$, where $u = e^2 / 4\pi\epsilon_0 a$ [28]. This value is $23 \text{ k}_B T$.

In conclusion, the recent identification of prenucleation clusters in calcium carbonate solutions suggests a new focus for research aimed at grasping the magnetic water treatment nettle. Barring some unforeseen resonance effect and consequent chemical change, mechanical stress on the charged ionic clusters due to the Lorentz force seems unlikely to deform them into a new structure that will be stable for many hours. Evidence that proton transport plays a key role in the magnetic field effect on calcium carbonate growth leads us to postulate transient dimeric structures of the protons in the prenucleation cluster, where the nuclear single:triplet ratio can be modified by the momentary passage through a nonuniform magnetic field. This can permit the formation of new ionic bonds, which are quasi-stable on a timescale of hours. The ionic structure of the pre-nucleation cluster is then supposed to influence its subsequent development into a calcite, vaterite or aragonite type of amorphous calcium carbonate (ACC). If the hypothesis is correct, the condition $C \approx 1$ in Equation (5) provides a design criterion for magnetic water treatment devices.

Provided the magnetic field effects on the crystallization of CaCO_3 can be put onto a sound scientific basis, there are appealing possibilities for new applications in important areas such as magnetically-controlled growth of calcium carbonate polytypes in biology [38–40], template-controlled carbonate growth [18,38] magnetic control of the chemistry of other species of ionic cluster in aqueous solution [21,28], magnetic influence of near-electrode reactions in electrochemistry including the evolution of H_2 gas [41], and influence on other solidification processes which involve proton transfer with dimer formation.

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