Emergence of spin singlets with inhomogeneous gaps in the kagome lattice Heisenberg antiferromagnets Zn-barlowite and herbertsmithite

Jiaming Wang1, Weishi Yuan1, Philip M. Singer2, Rebecca W. Smaha3,4, Wei He3,5, Jiajia Wen3, Young S. Lee3,6 and Takashi Imai3,7,8

The kagome Heisenberg antiferromagnet formed by frustrated spins arranged in a lattice of corner-sharing triangles is a prime candidate for hosting a quantum spin liquid (QSL) ground state consisting of entangled spin singlets1. However, the existence of various competing states makes the convincing theoretical prediction of the QSL ground state difficult2, calling for experimental clues from model materials. The kagome lattice materials Zn-barlowite (ZnCu3(OD)6FBr)3-5 and herbertsmithite (ZnCu3(OD)6Cl2)6-10 do not exhibit long-range order and are considered the best realizations of the kagome Heisenberg antiferromagnet known so far. Here we use 63Cu nuclear quadrupole resonance combined with the inverse Laplace transform11-13 to locally probe the inhomogeneity of spin singlets with spatially varying excitation gaps, but even at temperatures far below the super-exchange energy scale their fraction is limited to ~60% of the total spins. Theoretical models14,15 need to incorporate the role of disorder to account for the observed inhomogeneously gapped behaviour.

Experimental investigations of the kagome Heisenberg antiferromagnet often encounter complications as a result of undesirable long-range order, spin freezing or deviations from the ideal kagome structure16-21. By contrast, Zn-barlowite (ZnCu3(OD)6Cl2)4 and herbertsmithite (ZnCu3(OD)6Cl2)6 consist of spin-1/2 moments of Cu2+ ions arranged with perfect kagome symmetry, and remain paramagnetic even at T ≈100 K, where J ≈190 K is the Cu–Cu super-exchange interaction. Accordingly, experiments on these materials are expected to provide a platform for testing the theoretical ideas developed for the kagome Heisenberg antiferromagnet, such as determining whether the low-energy spin excitations are gapped or gapless.

A direct comparison of theory and observations on these materials is complicated because of disorder. Site-selective X-ray scattering experiments have demonstrated that their actual compositions are (Zn2+Cu2+)(Cu1+)(OD)6FBr (ref. 24) and (Zn2+Cu2+)(Cu1+)(OD)6Cl2 (ref. 25), because 5% or 15% excess Cu2+ impurities occupy the non-magnetic Zn2+ sites within the interlayers outside the kagome planes. On the other hand, the upper bound for non-magnetic Zn2+ defects occurring the Cu2+ sites within the kagome planes is ~1% (refs. 14,15). These interlayer defect concentrations are reproducible and were confirmed for samples from the same synthesis batches used in this study. The interlayer defect Cu2+ spins at Zn2+ sites interact with their six nearest-neighbour Cu2+ sites in the adjacent kagome planes, and disrupt the spin liquid ground state in their vicinity. In fact, earlier NMR Knight shift measurements at 1D (ref. 26) and 2D (ref. 27) in herbertsmithite showed that the local spin susceptibility χCu, is strongly enhanced in the immediate vicinity of the 15% interlayer Cu defects. Inelastic neutron scattering also reveals a peculiar ω/T-scaling behaviour in spin fluctuations at low energies below ω ≈0.1J, where ω represents the spin fluctuation frequency, suggesting the critical roles played by disorder 3. In view of the general tendency in disordered antiferromagnets for spin singlets to gradually emerge with spatially varying gaps4, disorder and the resultant inhomogeneity in these kagome materials must be taken into account when interpreting collective spin dynamics16-17.

In this Letter, we shed light on the magnetic inhomogeneity of these kagome materials by experimentally deducing the probability density function (that is, histogram) P(1/T1(ω)) of the distributed 63Cu nuclear spin-lattice relaxation rate 1/T1(ω) from the nuclear spin recovery curve M(t) based on the inverse Laplace transform (ILT) T1 analysis technique11-13, where T1 is the nuclear spin-lattice relaxation time. Below a temperature threshold of ~30 K, we uncover the gradual emergence of the magnetically inert spin-singlet Cu sites with spatially varying gaps, as evidenced by the gradual increase of the population of Cu sites with vanishing 1/T1Cu. Our observation of the robust spin-singlet signature, but only for a fraction fs < 0.6 of Cu sites even at T ≈0.01F, is direct evidence for a spatially inhomogeneous local response in the presence of disorder in these materials, showing the close competition of various ground states. These results also explain the seemingly contradictory interpretation of purely gapped or gapless behaviour based on 17O NMR results28-29, which did not properly account for inhomogeneity.

1/T1 is a local probe of spin fluctuations at the resonant frequency ω, where 1/T1 ∝χ(ω)/ω2, with Aω being the hyperfine coupling between the observed nuclear spin and electron spin, and
\(\chi'(\omega)\) the imaginary part of the local spin susceptibility. In general, 
\(1/T \propto |A_{\text{eff}}|/J\) for Heisenberg antiferromagnets at high temperatures \(^1\), and \(1/T\) remains roughly constant unless strong short-range order enhances \(1/T_1\) or a spin gap suppresses \(1/T\). The spatial proximity of the \(^{63}\text{Cu}\) nuclear spin and the spin-1/2 moment always enhances \(1/T_{1,\text{Cu}}\) measured at paramagnetic Cu\(^{2+}\) sites to large values of \(10^2\) to \(10^4\) s\(^{-1}\) in Heisenberg antiferromagnets (for example, refs. \(^{30–33}\)). When Cu\(^{2+}\) sites form magnetically inert singlet dimers, favoured by the non-frustrated geometry in two-leg spin-ladder \(\text{SrCu}_2(\text{BO}_3)_2\), \(^{63,65}\text{Cu}\) and \(^{79,81}\text{Br}\) NQR (both with nuclear spin \(1/2\)) responses would have a large concentration of Cu\(^{2+}\) defect spins in \(^{63}\text{Cu}\)\(_{(\text{OD})}\)\(_2\)Cl\(_2\). The enhancement of \(1/T\) for quadrupolar \(^{63}\text{Cu}\) and \(^{79}\text{Br}\) sites around 100 K in ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)FBr and around 50 K in ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)Cl\(_2\) is nearly identical for ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)FBr and ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)Cl\(_2\). This technique was initially developed two decades ago for NMR (\(I = 1/2\)). See Supplementary Section I for additional examples of \(M(t)\) and the temperature dependence of \(\beta\).

In Fig. 2a,b we summarize the stretched fit \(1/T_{1,\text{Cu}}\) measured with a short pulse separation time of \(\tau = 6\) ms (‘+’ symbols), \(1/T_{1,\text{Cu}}\) is nearly identical for ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)FBr and ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)Cl\(_2\) except below \(\sim 4\) K, where fluctuating hyperfine magnetic fields originating from the larger concentration of Cu\(^{2+}\) defect spins in ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)Cl\(_2\) enhance the floor value of \(1/T_{1,\text{Cu}}\). The enhancement of \(1/T\) observed for quadrupolar \(^{63}\text{Cu}\) and \(^{79}\text{Br}\) sites around \(40\) K in ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)FBr and around \(70\) K in ZnCu\(_3\)\(_{\langle \text{OD}\rangle}\)\(_2\)Cl\(_2\) is caused by the slowing of the fluctuating electric field gradient induced by the structural distortion near the defects \(^{34–35}\).

Unlike spin-singlet dimer materials \(^{31–33}\), \(1/T_{1,\text{Cu}}\) hovers at fairly large values of \(\sim 10^2\) to \(10^4\) s\(^{-1}\) below \(40\) K and hence does not hint at the presence of spin singlets. However, interpretation of \(1/T_{1,\text{Cu}}\) deduced from the conventional stretched fit requires caution, because one can easily overlook the presence of two distinct components of \(1/T\) (ref. \(^{12}\)). Without knowing the exact nature of the large distribution, it is risky to draw conclusions from \(1/T_{1,\text{Cu}}\). Indeed, this is where NMR research into disordered quantum materials used to run into difficulties.

There is, however, a way to deduce the histogram \(P(1/T_i)\) of the distribution of \(1/T_i\) directly from \(M(t)\) by taking advantage of the ILTT analysis technique based on Tikhonov regularization \(^{11–13}\). This technique was initially developed two decades ago for NMR research into petrophysics, but can easily be adapted to quantum materials \(^{32,33}\). In ILTT analysis, one assumes only that \(1/T_i\) is spatially distributed and \(M(t) = \sum P(1/T_i) (1 - 2\exp(-ct/T_i))\), \(1/T_0\) is the fitting value of the distribution \(1/T_i\), and \(P(1/T_i)\) represents the corresponding probability density for the nuclear spins to relax with \(1/T_i\). We numerically invert the discrete \(M(t)\) data based on ILT, and deduce the histogram \(P(1/T_i)\) of the distributed \(1/T_i\). We refer readers to a brief review in section II of ref. \(^{12}\) and its supplementary...
In Fig. 1g, we compare the stretched and ILT fits of $^{63}$Cu in ZnCu$_3$(OD)$_6$Cl$_2$. At 40 K, the distribution $P(1/T_{Cu})$ is a reasonably good approximation of $P(1/T_{Cu}^{\text{str}})$, as determined from the conventional stretched fit of $^{63}$Cu. This small value overestimates the intrinsic contributions from Cu$^{2+}$ spin fluctuations within the kagome plane, because the aforementioned Cu$^{2+}$ defect spins at Zn$^{2+}$ sites should induce constant background contributions. Such a small $1/T_{Cu}^{\text{str}}$ value of $\sim 20$ s$^{-1}$ or less was previously observed for Cu$^{2+}$ sites only in the gapped spin-singlet ground state of spin dimer materials$^{31-33}$. Therefore, we can attribute the split-off peak of $P(1/T_{Cu}^{\text{str}})$ to the emergent singlets, whereas the para peak represents Cu$^{2+}$ sites that have not yet been involved in singlets. ZnCu$_3$(OD)$_6$Cl$_2$ exhibits remarkably similar results, as shown in Figs. 2b,f and 3b, except that the higher defect concentration in ZnCu$_3$(OD)$_6$Cl$_2$ results in smearing of the $P(1/T_{Cu}^{\text{str}})$ curves and enhances the floor value of the singlet peak to $1/T_{Cu}^{\text{singlet}} \approx 80$ s$^{-1}$.

The integral of the $P(1/T_{Cu})$ curves in Fig. 3 is normalized to 1 so that the total probability is 1. Accordingly, the integrated area under the purple dashed curve centred at $1/T_{Cu}^{\text{singlet}}$ represents the fraction $f_s$ of Cu sites involved in the singlets. We summarize the temperature dependence of $f_s$ in Fig. 4, where $f_s$ shows nearly identical behaviour for ZnCu$_3$(OD)$_6$FBr and ZnCu$_3$(OD)$_6$Cl$_2$, and remains finite up to $\sim 30$ K. A na"ive extrapolation of $f_s$ to $T = 0$ may reach close to 100%. However, $f_s$ in Fig. 4 should be considered the upper bound, because we measured $1/T_{Cu}$ with a finite $\tau = 6 \mu$s, which tends to underestimate faster-relaxing components. We also note that muon spin resonance detected slow spin dynamics in these materials at temperatures below roughly 6 K (ref. 3), where some $^{63}$Cu and $^{79}$Br NQR signal intensity is lost, as shown in Supplementary Section I. These findings suggest incipient freezing of some Cu$^{2+}$ spins. Therefore, the $f_s$ results in this temperature regime represent the fraction of singlet Cu$^{2+}$ sites in a region that are not about to freeze.

**Fig. 2** $1/T$, and its distribution $P(1/T)$. a-d, $1/T_{Cu}^\text{str}$ (‘+’ symbols), as determined from the conventional stretched fit of $^{63}$Cu (a), $^{79}$Br (c) and $^{19}$F (d) sites in ZnCu$_3$(OD)$_6$FBr, and $^{63}$Cu (b) sites in ZnCu$_3$(OD)$_6$Cl$_2$. Also compared in a-d are the centre-of-gravity $1/T_{Cu}^\text{str}$ (filled circles), paramagnetic $1/T_{Cu}^\text{para}$ (open squares) and singlet $1/T_{Cu}^\text{singlet}$ (open circles), as determined from the density distribution $P(1/T)$. Error bars for $1/T_{Cu}^\text{para}$ and $1/T_{Cu}^\text{singlet}$ represent the absolute maximum/minimum in the peak locations of the double Gaussian fit of $P(1/T)$. e-h, Colour contour plots of $P(1/T)$ corresponding to the results presented in a-d. Colour scales are provided above e-h.

...
The fact that $f_s$ does not exceed 60% even at $T \approx 0.01$J indicates that theoretical models derived for the pristine kagome Heisenberg antiferromagnet are insufficient to account for the low-energy properties of these kagome materials with disorder. Instead, our $P(1/T_{1\text{Cu}})$ results indicate that spin singlets gradually emerge with spatially varying gaps. A variety of interesting theoretical scenarios may result from the disorder\textsuperscript{14–17}, but the presence of a spin gap in part of the sample is clear. Although it is not straightforward to extrapolate this finding to the disorder-free limit, it seems unlikely that the gap is induced by disorder, in view of the fact that disorder may result from the disorder\textsuperscript{14–17}, but the presence of a spin gap in part of the sample is clear. Although it is not straightforward to extrapolate this finding to the disorder-free limit, it seems unlikely that the gap is induced by disorder, in view of the fact that disorder generally generates low-lying excitations. It is worth noting that if these materials are a realization of a QSL with a uniform gap $\Delta$, $P(1/T_{1\text{Cu}})$ should have a single peak representing 100% of Cu sites, and the peak $1/T_{1\text{Cu}}$ value should exhibit activated behaviour for that uniform gap $\Delta$. We also note that the apparent linear behaviour of $1/T_{1\text{Cu}}$ in the log–log plot in Fig. 2b could be misinterpreted as a power-law behaviour of $1/T_{1\text{Cu}} \sim T^\alpha$ ($\alpha < 1$) expected for Dirac fermions in gapless spin liquids\textsuperscript{16}, but this is illusory and disappears when confronted with the actual distribution of $1/T_{1\text{Cu}}$. In reality, neither $1/T_{1\text{Cu}}$ nor $1/T_{1\text{Cu}}^{\text{Singlet}}$ obeys such a power law for either ZnCu$_3$(OD)$_6$Cl$_2$ or ZnCu$_3$(OD)$_6$FBr. Therefore, the fully gapless QSL scenario advocated previously based on an apparent power-law behaviour of $1/T_{1\text{Cu}}$ observed for $^{17}$O sites\textsuperscript{16} is ruled out by $P(1/T_{1\text{Cu}})$.

NMR data at other sites provide additional clues about the nature of the inhomogeneously gapped regions of the kagome planes. As shown in Fig. 1f, $^{79}$Br and $^{19}$F sites are equidistant, with 6 and 12 Cu$^{2+}$ sites, respectively, and hence $1/T_{1\text{Cu}}$ probes their average behaviour. If the spin singlets form a valence-bond solid consisting of large clusters, as depicted in Fig. 1c, some $^{79}$Br and/or $^{19}$F sites would be surrounded by magnetically inert spins and exhibit a split-off peak in $P(1/T_{1\text{Cu}}^{\text{Singlet}})$. The absence of such a signature in $P(1/T_{1\text{Cu}}^{\text{Singlet}})$ suggests that $^{79}$Br and $^{19}$F sites are surrounded randomly by both spin singlets and paramagnetic spins, as opposed to the dimer order expected for a valence-bond crystal. Previous $^{17}$O NMR results\textsuperscript{16} also corroborate the present findings. Notice that each $^{17}$O site is sandwiched between two Cu spins—when a certain fraction $f_{\text{s}}$ of Cu spins form the singlets when temperatures fall below $\sim 30$ K, a corresponding fraction of $^{17}$O sites are within the singlets and become magnetically inert. This naturally explains why the $^{17}$O NMR Knight shift $\Gamma_1$ defined at the centre peak of the extremely broad $^{17}$O NMR line begins to
exhibit a gapped behaviour around 30 K (refs. 9,10) with a small gap of $\Delta \approx 10$ K (ref. 10). This is also supported by the gapped behaviour of 1/2 electrons observed for the second upper satellite quadrupole transition of $^{17}$O sites, which was narrowed and isolated by using a low magnetic field of 3.2 T to avoid contamination by other quadrupole satellites. The observed gap at $^{64}$Cu and $^{17}$O sites is attributed to the break-up energy of the singlets and other local excitations, and does not represent a uniform gap throughout the kagome planes. In fact, a fraction $1 - f_s$ of Cu sites remain paramagnetic with constant 1/T$_{\text{Curie}}$ down to $T = 0.1$ K, and these Cu sites lack a spin excitation gap. This is also in agreement with the recent $^{17}$K results determined for $^{17}$O sites with very fast relaxation rates 10. Further microscopic theories based on the specific disorder present in the materials are necessary to fully understand the quantitative aspect of $f_s$, as well as the origins of the observed gap and its spatial distribution.

Online content
Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41567-021-01310-3.

Received: 5 October 2020; Accepted: 22 June 2021; Published online: 5 August 2021

References
1. Balents, L. Spin liquids in frustrated magnets. Nature 464, 199–208 (2010).
2. Broholm, C. et al. Quantum spin liquids. Science 367, eaay0668 (2020).
3. Feng, Z. et al. Gapped spin-1/2 spinon excitations in a new kagome quantum spin liquid compound Cu$_3$Zn(OH)$_3$FBr. Chin. Phys. Lett. 34, 077502 (2017).
4. Smaha, R. W. et al. Materializing rival ground states in the barlowite family of kagome magnets: quantum spin liquids, spin ordered and valence bond crystal states. npj Quantum Mater. 5, 23 (2020).
5. Tustain, K. et al. From magnetic order to quantum disorder: a μSR study of the Zn-barlowite series of $S = 1/2$ kagomé antiferromagnets, Zn$_3$Cu$_{6-x}$-(OH)$_x$FBr. Nature Commun. 5, 74 (2020).
6. Shores, M. P., Nytko, E. A., Bartlett, B. M. & Nocera, D. G. A structurally perfect $S = 1/2$ kagomé antiferromagnet. J. Am. Chem. Soc. 127, 13462–13463 (2005).
7. Helton, J. S. et al. Spin dynamics of the spin-1/2 kagome lattice antiferromagnet ZnCu$_3$(OH)$_3$Cl$_2$. Phys. Rev. Lett. 98, 107204 (2007).
8. Han, T.-H. et al. Fractionalized excitations in the spin–liquid state of a kagome-lattice antiferromagnet. Nature 492, 406–410 (2012).
9. Fu, M., Imai, T., Han, T.-H. & Lee, Y. S. Evidence for a gapped spin–liquid ground state in a kagome Heisenberg antiferromagnet. Science 350, 655 (2015).
10. Khunia, P. et al. Gapless ground state in the archetypical quantum kagome antiferromagnet ZnCu$_3$(OH)$_3$Cl$_2$. Nat. Phys. 16, 469–474 (2020).
11. Song, Y. Q. et al. $T_1$–$T_2$ correlation spectra obtained using a fast two-dimensional Laplace inversion. J. Magn. Res. 154, 261–268 (2002).
12. Singer, P. M., Arsenault, A., Imai, T. & Fujita, M. $^{133}$La NMR investigation of the interplay between lattice, charge, and spin dynamics in the charge-ordered high-$T_c$ cuprate La$_{2-x}$Ba$_{x}$CuO$_4$. Phys. Rev. B 101, 174508 (2020).

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2021
Methods
We synthesized deuterated (D = 2H) powder samples of ZnCu3(OD)6FBr and ZnCu3(OD)6Cl2 based on the procedures described in detail in refs. 4, 6. We confirmed the sample quality based on powder X-ray diffraction measurements. We also confirmed the interlayer defect concentrations and absence of observable in-plane defects based on site-selective X-ray studies and inductively coupled plasma (ICP) chemical analysis for samples from the same synthesis batches used in this study7. We conducted spin echo NMR and NQR measurements using standard pulsed NMR spectrometers. Typical pulse widths were ~2.5 and 5 μs for 90° and 180° radiofrequency pulses, respectively. We measured the NQR lineshapes in Fig. 1d using a fixed pulse separation time of τ = 15 μs and normalized the spin echo intensity for the sensitivity by dividing by the frequency squared. We assigned the NQR peaks of the 63Cu, 65Cu, 79Br and 81Br isotopes based on the ratio of the peak frequencies, which is proportional to the ratio of the nuclear quadrupole moment (63Q/65Q = 0.927 and 81Q/79Q = 0.837). We conducted all the 1/T1 measurements by applying an inversion pulse prior to the spin echo sequence. For 1/T1Cu measurements, we used a short pulse separation time of τ = 6 μs between the 90° and 180° pulses unless otherwise noted. We conducted the ILT analysis of M(t) based on the established procedures described in ref. 12. We also confirmed the validity of the ILT results by two additional checks: (1) two-component analysis of M(t) in the time domain led to consistent results and (2) 1/T1Cu measured with a long r = 30 μs agreed with 1/T1Cu,m-temp. See Supplementary Sections III and IV for additional details. We chose to conduct the 19F NMR measurements of 1/T1 in an external magnetic field of 0.72 T so that the 19F resonant frequency coincided with the 79Br NQR peak frequency in zero field. This is because the enhancement of 1/T1 due to a fluctuating electric field gradient at the 35Cl sites of ZnCu3(OH)6Cl2 is known to depend mildly on frequency24. The absence of a peak in 1/T1 around 100 K in Fig. 2d for non-quadrupolar 19F sites, as well as the isotope ratio of 1/T1 between 79Br and 81Br in Supplementary Section II, confirmed that the large enhancement of 1/T1, around 100 K is quadrupolar in nature and extrinsic to spin physics. We confirmed that the 19F Knight shift measured at 0.72 T agreed well with the higher-field results above ~10 K (ref. 12). However, the dramatic line broadening in 0.72 T overwhelmed the small Knight shift at lower temperatures and made accurate determination of the latter difficult.

Data availability
The datasets generated during the current study are available from the corresponding author on reasonable request.

Acknowledgements
T.I. thanks T. Sakai, K. Uematsu, R. R. P. Singh, I. Kimchi, P. A. Lee and S. Sachdev for helpful communications, and P. Dube and R. Giannetta for technical assistance. The work at McMaster was supported by NSERC (T.I.). P.M.S. was supported by the Rice University Consortium for Processes in Porous Media. The work at Stanford and SLAC (sample synthesis and characterization) was supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under contract no. DE-AC02-76SF00515 (Y.S.L and J. Wen). R.W.S. was supported by the US Department of Defense (DoD) through the National Defense Science and Engineering Graduate Fellowship (NDSEG) Program as well as an NSF Graduate Research Fellowship (DGE-1656518).

Author contributions
T.I. and Y.S.L conceived the project. R.W.S., W.H., J. Wen and Y.S.L synthesized and characterized the samples. J. Wang, W.Y., P.M.S. and T.I. carried out the NMR measurements and data analysis. All authors contributed to the writing and editing of the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41567-021-01310-3.
Correspondence and requests for materials should be addressed to T.I.

Peer review information Nature Physics thanks Martin Klanjsek and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.