Materials, Energy and Life:
Research Using Intense Magnetic Fields

Greg Boebinger      www.magnet.fsu.edu
In 2012, the MagLab hosted experiments by more than 1350 users from 159 institutions across the United States... and a total of 277 institutions throughout the world.
The MagLab is its User Program

MagLab users publish about 440 refereed publications annually:

**2009-2013 Publications**

<table>
<thead>
<tr>
<th>Publications</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>2200</td>
</tr>
<tr>
<td>PNAS</td>
<td>28</td>
</tr>
<tr>
<td>Nature Journals</td>
<td>63</td>
</tr>
<tr>
<td>Physical Review Letters</td>
<td>147</td>
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<tr>
<td>Physical Review B</td>
<td>318</td>
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<tr>
<td>PRB (Rapid Comm)</td>
<td>47</td>
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<tr>
<td>JACS</td>
<td>59</td>
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</tbody>
</table>
Note: At the MagLab, roughly 50% of the “Chemistry” category is Solid State Chemistry.
MagLab Technology Leads the World for Highest Magnetic Fields Achieved

PULSED MAGNETS
- Short Pulse (1-10 msec)
- Long Pulse (100-5000 msec)

CONTINUOUS (DC) MAGNETS
- Hybrid (Resistive + Superconducting)
- All Resistive

SUPERCONDUCTING MAGNETS
- Demonstration Test Coils
- Commercial Magnet Systems

Records when MagLab was created (1990):
- 68T MIT
- 40T Amsterdam
- 31T Grenoble
- 24T Grenoble
- 17.5T IGC, Inc.
- 101T MagLab
- 60T MagLab
- 45T MagLab
- 36T MagLab
- 35T MagLab
- 23.4T Bruker, Inc.*

68T MIT

MagLab Technology  Leads the World for Highest Magnetic Fields Achieved
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Current Records
- 101T MagLab
- 60T MagLab
- 45T MagLab
- 37.5T Nijmegen
- 36T MagLab
- 35T MagLab
- 23.4T Bruker, Inc.*

Records when MagLab was created (1990)
- 68T MIT
- 40T Amsterdam
- 31T Grenoble
- 24T Grenoble
- 17.5T IGC, Inc.

22 years later...

Timeline:
- 1950-1990
- 1990-2010
Superconducting Magnet Technology
Watching a revolution in real time

Superconducting Magnets
- Demonstration Test Coils
- Commercial Magnet Systems

SUPERCONDUCTING MAGNETS
- 23.5 T (1GHz NMR) Nb$_3$-Sn
  Superconducting Magnets
  (Manufactured Commercially)
- 35 T Proof-of-Principle Demo
  (4T HTS Test Coil in a
  31T Background Magnetic Field)

0T 5T 10T 15T 20T 25T 30T 35T

- Nb-Ti
- Nb$_3$-Sn

ϕ 39 mm
A Decade of MagLab Collaborations on High-Tc Test Coils

First HTS Coil operating above 30T (red) also demonstrates a FIVE-FOLD increase in current density (blue) ...
...more compact magnets are MUCH cheaper!
The 2013 National Research Council “MagSci” Report is extremely supportive of the MagLab

**EXECUTIVE SUMMARY:**

Continued advancement in high-magnetic-field science requires substantial investments in magnets with enhanced capabilities. The NHMFL in the United States is presently considered to be the world leader in both advancing magnet technology and high-field science.

Magnet projects must include materials development and magnet component test-bed facilities. Most MagSci magnets require HTS materials and technology development.

<table>
<thead>
<tr>
<th><strong>MagSci Recommended Magnet Projects</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 30-37 T (1.3 – 1.6 GHz) NMR Magnet</td>
</tr>
<tr>
<td>2: 150 T (msec) pulse for thermal transport &amp; optical experiments</td>
</tr>
<tr>
<td>3a: 40 T pulse, 30 sec rep rate for neutrons and/or x-rays</td>
</tr>
<tr>
<td>3b: 40 T HTS SC magnet for neutrons (and/or x-rays)</td>
</tr>
<tr>
<td>3c: 25-35T Series Connect Hybrid for neutrons and/or x-rays</td>
</tr>
<tr>
<td>4: Regional 32 T – 40T SC facilities (including at the MagLab)</td>
</tr>
<tr>
<td>5: 60 T hybrid magnet</td>
</tr>
<tr>
<td>6: 20 T large-animal &amp; human MRI</td>
</tr>
<tr>
<td>7: Axion &amp; other detectors, fusion, <strong>particle accelerators</strong>, radiotherapy.</td>
</tr>
</tbody>
</table>
Higher $T_c$ superconducting magnets are a persistent dream of the condensed matter community......

Cuprates can superconduct up to 130 K

Applications in liquid nitrogen at 77 K are still very rare

More than 95% of all superconductor sold is still Nb-Ti with $T_c$ of 9 K

Applications are determined by high $J_c$, $J_e$ and $H_{irr}$ rather than by high $T_c$

Conductors of exotic materials are difficult!

The dream: escape from bottom left corner to the upper and the right......
ITER has made tonnage breakout for Nb$_3$Sn – both CERN and the MagLab are assisting ITER

SUPERCONDUCTIVITY IN Nb$_3$Sn AT HIGH CURRENT DENSITY IN A MAGNETIC FIELD OF 88 kgauss
J. E. Kunzler, E. Buehler, F. S. L. Hsu, and J. H. Wernick
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received January 9, 1961)

We have observed superconductivity in Nb$_3$Sn at average current densities exceeding 100 000 amperes/cm$^2$ in magnetic fields as large as 88 kgauss. The nature of the variation of the critical current (the maximum current at a given field for which there is no energy dissipation) with magnetic field shows that superconductivity extends to still higher fields. Existing theory does not account for these observations. In addition to some remarkable implications concerning superconductivity, these observations suggest the feasibility of constructing superconducting solenoid magnets capable of fields approaching 100 kgauss, such as are desired as laboratory facilities and for containing plasmas for nuclear fusion reactions.\textsuperscript{1,2}

The highest values of critical magnetic fields previously reported for high current densities

ITER uses 600 tonnes of Nb$_3$Sn

1. Bi-2223 – the first HTS conductor – uniaxial texture developed by deformation and reaction (1995- today)

2. REBCO coated conductor – extreme texture (single crystal by the mile) – for maximum GB transparency (2007)

Nb47Ti conductor - thousands of 8 μm diameter Nb47Ti filaments in pure Cu (0.8 mm dia.), easily cabled to operate at 10-100 kA
Applications are determined by high $J_c$, $J_e$ and $H_{irr}$ rather than by high $T_c$.

Conductors of exotic materials are difficult!
High-Tc Superconducting Magnet Technology: Building a 32T All-Superconducting REBCO Magnet

- 17 T / 32 mm bore REBCO coils
- 15 T
- 250 mm bore LTS magnet
- Dilution refrigerator
1. Bi-2223 – the first HTS conductor – uniaxial texture developed by deformation and reaction (1995- today)

2. Bi-2212 – high \(J_c\) without macroscopic texture (2012)!

3. REBCO coated conductor – extreme texture (single crystal by the mile) – for maximum GB transparency (2007)

4. Nb47Ti conductor - thousands of 8 \(\mu\)m diameter Nb47Ti filaments in pure Cu (0.8 mm dia.), easily cabled to operate at 10-100 kA

NB47Ti conductor

LHC conductor

HTS Magnet Conductors Now
Bi-2212 –developed by NHMFL, DOE-HEP labs and Oxford Superconducting Technology (OST) – twisted, round, filamentary conductor fully competitive with any other HTS in $J_E$

- Fine filament twisted conductor is ideal for high homogeneity NMR and accelerator magnets

From the cover of the MagSci report

Bi-2212 conductor support by DOE–OHEP: an outcome of Bismuth Strand and Cable Collaboration (BSCCo)
Large magnets are better protected when cabled: Substantial R&D required to develop HTS cabling technologies.

- Cables vital for 60 T hybrid at the NHMFL, an LHC energy upgrade and a neutrino machine based on a Muon Collider at Fermilab.

- Easy path to 2212 cables through the standard Rutherford cable.

- REBCO cables are harder (Coated Conductor is a single filament) - but possible (IRL, KIT, CORC, twisted stack (MIT)).

- Bi-2212 Rutherford cables (Arno Godeke LBNL) with mullite insulation sleeve.

- REBCO coated conductor cable wound in many layers helically on a round form.

- Other variants too: e.g. Roebel cable.
Size and field trade off for the LHC

- **LHC**
  - 27 km, 8.33 T
  - 14 TeV (c.o.m.)

- **HE-LHC**
  - 27 km, 20 T
  - 33 TeV (c.o.m.)

- **VHE-LHC**
  - 80 km, 20 T
  - 100 TeV (c.o.m.)

- **VHE-LHC**
  - 100 km, 16 T
  - 100 TeV (c.o.m.)

8 T: Nb-Ti, 16 T: Nb$_3$Sn, 20 T: HTS

Luca Bottura (CERN) – MT23 talk
High Magnetic Fields and Materials
Graphene, Fe-based superconductors, Quantum oscillations in cuprate superconductors, Topological insulators, Molecular magnets, Model magnetic systems, Frustrated magnets, Magnetic Bose-Einstein Condensates, Qubits, Energy-related materials, Petroleum, Natural Products, Bio-macromolecular complexes and the Brain
First Key Ingredient for (‘Cuprate’) High-Temperature Superconductors:

the Copper – Oxygen Plane

The 2D Copper-Oxygen Plane...
...the playground of high-temperature superconductivity

With one electron on each Copper atom, the electrons cannot move...
...and you have an insulator
Second Key Ingredient for (‘Cuprate’) High-Temperature Superconductors:

Removing electrons from the Copper – Oxygen Plane

Remove ~5% to ~27% of the electrons…

…and you have a HIGH-TEMPERATURE SUPERCONDUCTOR

For more than a dozen different materials, the same 16% doping…

...optimizes superconductivity (highest transition temperature)
Large Fermi Surface in Tl-2201 in the overdoped regime

Original measurement using Angle-Dependent Magneto-resistance Oscillations:
N.E. Hussey, M. Abdel-Jawad, A. Carrington, A.P. Mackenzie, L. Balicas,

FIG. 1. (Color online) Fast Fourier transform of torque data between 38 and 45 T for Tl26K (red) and Tl10Ka (blue) samples. The data were taken at \(T=0.35\) K. The inset shows the raw data for the two samples.

A.F. Bangura, P.M.C. Rourke, T.M. Benseman, M. Matusiak, J.R. Cooper, N.E. Hussey, and A. Carrington
Fermiology and electronic homogeneity of the superconducting overdoped cuprate \(\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}\)


Superconductivity is Stabilized Near Quantum Critical Points, but no one knows why.


\[ \text{Celn}_3 \]
\[ \text{a Heavy Fermion Compound with Superconducting } T_c < 1 \text{ K} \]

\[ \text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2 \]

Determination of the phase diagram of the electron doped superconductor \( \text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2 \)
Superconductivity is Stabilized Near Quantum Critical Points, but no one knows why.


Hole-doped High-Temperature Superconducting Cuprate Maximum $T_c \sim 40-150K$

$\text{CeIn}_3$

a Heavy Fermion Compound with Superconducting $T_c < 1K$
Graphene, Fe-based superconductors, Quantum oscillations in cuprate superconductors, Topological insulators, Molecular magnets, Model magnetic systems, Frustrated magnets, Magnetic Bose-Einstein Condensates, Qubits, Energy-related materials, Petroleum, Natural Products, Bio-macromolecular complexes and the Brain
Materials Research on Chinese Terracotta Warriors (479-221 BC)
Saving Lives for more than 2000 Years

Terracotta Army to protect the emperor in the afterlife...instead of the real army

J. Zuo et al., J. Raman Spectrosc. 34, 121 (2003)

Calcite - CaCO₃
Bone White - Ca₅(CO₃)₂(OH)₂
White Lead – 2Pb(CO₃)₂·Pb(OH)₂
Soot - carbon black

Han Purple*** - BaCuSi₂O₆

Cinnabar - HgS
Hematite - Fe₂O₃
Red Lead – Pb₃O₄
Malachite – Cu₂CO₃(OH)₂

Han Blue*** – BaCuSi₄O₁₀

*** man-made pigments
BaCuSi$_2$O$_6$: A quasi-2D magnetic insulator with a gapped spin dimer ground state.

Magnetic fields create a gas of bosonic spin triplet excitations, called triplons.

Slow increase in MAGNETIZATION is evidence of electron spin correlations.

Lambda transition in SPECIFIC HEAT due to Bose condensation of triplons.
SrCu$_2$(BO$_3$)$_2$ realizes the “Shastry-Sutherland Model”: Orthogonal spin dimers on square lattice

- Dimers are *coupled*; magnetization increases in a complex series of plateaus as *stable magnetic textures* are formed.

Marcelo Jaime, Ramzy Daou, Scott A. Crooker, Franziska Weickert, Atsuko Uchida, Adrian E. Feiguin, Cristian D. Batista, Hanna A. Dabkowska, and Bruce D. Gaulin

*PNAS*, (July 2012)
• SrCu$_2$(BO$_3$)$_2$ realizes the “Shastry-Sutherland Model”: *Orthogonal spin dimers on square lattice*

• Dimers are *coupled*; magnetization increases in a complex series of plateaus as *stable magnetic textures* are formed

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**March 2012: First time 100T was achieved non-destructively...**

The 100T pulse yielded a PNAS, 2 PRL’s, 2 PRB(Rapid Comm)’s and an Inorg. Chem. paper

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Marcelo Jaime, Ramzy Daou, Scott A. Crooker, Franziska Weickert, Atsuko Uchida, Adrian E. Feiguin, Cristian D. Batista, Hanna A. Dabkowska, and Bruce D. Gaulin

*PNAS, (July 2012)*
High Magnetic Fields and Energy
Graphene, Fe-based superconductors,
Quantum oscillations in cuprate superconductors,
Topological insulators, Molecular magnets,
Model magnetic systems, Frustrated magnets,
Magnetic Bose-Einstein Condensates, Qubits,
**Energy-related materials**, Petroleum, Natural Products,
Bio-macromolecular complexes and the Brain
High-field EPR probes charge carriers in plastic solar cells

If the unpaired electron is delocalized over a large volume, its g factor is nearly that of a free electron (2.0023 and isotropic). As such, high magnetic fields are required to measure the g-tensor in carbon-centered radicals in organic photovoltaics.
A STRAFI probe was designed to image solid and liquid materials containing quadrupolar nuclei using the fringe field of a superconducting magnet.

Reveals formation and changes of irreversible microstructures of the Li components in the interface between electrolyte and electrodes

Reveals a non-uniform Li-ion distribution in the graphite for the first time
Graphene, Fe-based superconductors, Quantum oscillations in cuprate superconductors, Topological insulators, Molecular magnets, Model magnetic systems, Frustrated magnets, Magnetic Bose-Einstein Condensates, Qubits, Energy-related materials, Petroleum, Natural Products, Bio-macromolecular complexes and the Brain
Ion Cyclotron Resonance: Mass Spectroscopy

With a 14 T high-homogeneity wide-bore magnet, 100 part-per-billion mass resolution and accuracy to analyze petroleum and metabolic compounds.

More than 100,000 different molecules in oil and different for each oil well.

Improved Resolution with FT-ICR

QqTOF (the primary competing technique)

Mass in Dalton (a.m.u.)

$\text{C}_7\text{H}_8\text{N}_5\text{O}^+$
$m/z$ 178.07234

$^{12}\text{C}_7^{13}\text{C}_1\text{H}_9\text{N}_4\text{O}^+$
$m/z$ 178.08044

$\text{C}_8\text{H}_8\text{N}_3\text{O}_2^+$
$m/z$ 178.06110

$\text{C}_8\text{H}_{10}\text{N}_4\text{O}^{++}$
$m/z$ 178.08491
Ion Cyclotron Resonance (ICR) can develop a “fingerprint” of the Deepwater Horizon oil by identifying 10,000’s of compounds in each sample.

The MagLab’s 9.4T ICR magnet can resolve 0.003 mDa and therefore can distinguish C$_3$ from SH$_4$ (greater than one part in 100,000 resolution) to allow for sulfur differentiation from pure hydrocarbons….the ability that launches “PETROLEOIMICS”
Ion Cyclotron Resonance (ICR) can develop a “fingerprint” of the Deepwater Horizon oil by identifying 10,000’s of compounds in each sample.

The MagLab’s 9.4T ICR magnet can resolve 0.003 mDa and therefore can distinguish C₃ from SH₄ (greater than one part in 100,000 resolution) to allow for sulfur differentiation from pure hydrocarbons….the ability that launches “PETROLEOMICS”

One might have expected to see fewer compounds in a weathered tar ball, because all volatile compounds would have evaporated.

Instead there are three times as many compounds, because bacteria and sunlight have led to the oxidization of many compounds.

High magnetic fields provide unique opportunities to probe the environmental fate of spilled oil, toxicology, and molecular modeling of biotic/abiotic weathering.

**Facilities:** NHMFL Ion Cyclotron Resonance Facility
**Citation:** Expansion of the Analytical Window for Oil Spill Characterization by Ultrahigh Resolution Mass Spectrometry: Beyond Gas Chromatography; McKenna, A.M.; Nelson, R.K.; Reddy, C.M.; Savory, J.J.; Kaiser, N.K.; Fitzsimmons, J.E.; Marshall, A.G. and Rodgers, R.P.; Environmental Science & Technology, 47, 7530-7539 (2013)
Inventing ‘Petroleomics’: Quantitative Analysis of Petroleum

More than 100,000 different molecules in oil and different for each oil well

...what is in the crude that clogs the oil pipelines? (costing $10,000,000 a day)

NOT polymerization... rather a physical entanglement of relatively small molecules

...how do we make useful fuel from this low grade crude? (we have enough of this stuff to achieve energy independence)

...what cyclic compounds are in this “residue”? ...and sulfur ligands / acids / <insert word here> (individualize refinement and mitigate pollution)
High Magnetic Fields and Life
11.4T MRI Magnet
400mm warm bore

Advanced Magnetic Resonance Imaging and Spectroscopy Facility

Graphene, Fe-based superconductors, Quantum oscillations in cuprate superconductors, Topological insulators, Molecular magnets, Model magnetic systems, Frustrated magnets, Magnetic Bose-Einstein Condensates, Qubits, Energy-related materials, Petroleum, Natural Products, Bio-macromolecular complexes and the Brain
Chemical Warfare in the Natural World: Solving Molecular Structures of Ultra-Small Samples

• High Quality NMR Spectrum from a single milking of a single walking stick... no purification... 10nL sample (0.1mm)^3

and from an unusual shell-less mollusk on the coral reef...
National High Magnetic Field Laboratory

Florida State University

Graphene, Fe-based superconductors,
Quantum oscillations in cuprate superconductors,
Topological insulators, Molecular magnets,
Model magnetic systems, Frustrated magnets,
Magnetic Bose-Einstein Condensates, Qubits,
Energy-related materials, Petroleum, Natural Products,
**Bio-macromolecular complexes** and the Brain
Fighting Viruses: Plugging the RNA Channels

Structure of Macro-bio-assemblies: too big for X-rays alone to solve

Ion Cyclotron Resonance weighs the pieces of the RNA channel to detect how much deuterium (heavy hydrogen) has exchanged with the hydrogen

Hydrogen/Deuterium Exchange Rate reveals which side of the RNA channel is on the virus exterior

> 100 \, h^{-1} \text{ FAST}
10 \, h^{-1} - 100 \, h^{-1}
1 \, h^{-1} - 10 \, h^{-1}
0.1 \, h^{-1} - 1 \, h^{-1}
< 0.1 \, h^{-1} \text{ SLOW}

WHICH surface is the EXTERIOR of the virus?

This is the EXTERIOR...
...design a drug to attack HERE
First Fully Functional Membrane Protein Structure Measured in a Native-Like Membrane Environment

A collaboration:
D. Busath, Dept. of Physiology and Developmental Biology, BYU; H.-X. Zhou, Dept. of Physics, FSU

The largest structure solved by ssNMR (20 kDa)

Sharma et al., 2010 Science

This would not be possible without the highest fields and Low-E probes.
Quadrupolar Nuclei: the REST of the Periodic Table

Elements with:
- Only $I = \frac{1}{2}$ nuclear spins
- Quadrupolar nuclei (i.e. $I > \frac{1}{2}$)

Quadrupolar Nuclei: the REST of the Periodic Table

NMR of New Materials in DC Powered Magnets

- $I = 1$: $^2\text{H}$, $^6\text{Li}$, $^14\text{N}$
- $I = 3/2$: $^7\text{Li}$, $^11\text{B}$, $^23\text{Na}$, $^{69,71}\text{Ga}$, $^{87}\text{Rb}$...
- $I = 5/2$: $^{17}\text{O}$, $^{25}\text{Mg}$, $^{27}\text{Al}$, $^{47}\text{Ti}$, $^{67}\text{Zn}$...

- **Catalysts:** surface chemistry
- **Porous materials:** clays and zeolites
- **Batteries and fuel cells:** ion transport
The nervous system is dependent upon the proper function of ion channels, pores in cell membranes that are able to transport ions, such as potassium and sodium, into and out of the cell.

Because $^{17}$O is a quadrupolar nucleus, it is a very sensitive indicator of the electric fields of nearby ions.

At 21.1 teslas in the 900MHz magnet we can detect NMR line shifts due to the electric fields of potassium ions at particular sites along the ion channel.

The shift in the $^{17}$O NMR signal upon detecting the electric field from a nearby potassium ion ($K^+$).
Graphene, Fe-based superconductors, Quantum oscillations in cuprate superconductors, Topological insulators, Molecular magnets, Model magnetic systems, Frustrated magnets, Magnetic Bose-Einstein Condensates, Qubits, Energy-related materials, Petroleum, Natural Products, Bio-macromolecular complexes and the Brain
Imaging has improved from frog ovum to rat neuron in 20 years ($10^6 : 1$ volume ratio)

...and now sub-cellular structures: the cell’s nucleus...and starting to resolve the 10,000 nucleoi *inside* the cell’s nucleus
Water diffusion is easy along nerves, difficult between nerves.

Healthy (left) and Damaged (right)
MOUSE SPINAL CORDS

Water pathways in the HUMAN BRAIN can now resolve bundles as small as 100 axons
Quadrupolar Nuclei Revisited for MRI

Elements with:

- Only I = 1/2 nuclear spins
- Quadrupolar nuclei (i.e. I > 1/2)

|        | H 2 | Li 6,7 | Be 9 | Na 23 | Mg 25 | K 39,43 | Ca 45 | Sc 45 | Ti 47,49 | V 50,51 | Cr 53 | Mn 55 | Fe 59 | Co 61 | Ni 61 | Cu 63,65 | Zn 67 | Ga 69,71 | Ge 73 | As 75 | Se 79,81 | Br 79,81 | Kr 83 | Rb 85,87 | Sr 87 | Y 91 | Zr 93 | Nb 93 | Mo 97 | Tc 99,101 | Ru 99,101 | Rh 105 | Pd 105 | Ag 113,115 | Cd 113,115 | In 113,115 | Sn 113,115 | Sb 121,123 | Te 127 | I 127 | Xe 129,131 | Cs 133 | Ba 135,138 | La 138,141 | Hf 177,181 | Ta 181,184 | W 185,187 | Re 185,187 | Os 187,189 | Ir 191,193 | Pt 197 | Au 197,198 | Hg 201 | Tl 201,203 | Pb 201,203 | Bi 201,203 | Po 204 | At 205,207 | Rn 222 |
|        |     |        |      |       |       |         |       |       |          |        |       |       |       |       |         |       |         |       |       |         |        |       |         |       |       |            |         |       |       |       |       |       |         |            |         |       |       |            |         |       |       |       |       |       |

Second Generation MRI: because you’re not just water and fat
Rapid Assessment of Chemotherapy using Sodium MRI

In vivo $^{23}$Na Images of mouse brain
Sodium MRI is *thousands of times more difficult* than ordinary Hydrogen MRI

Sodium ($^{23}$Na) inside the cells is a biomarker for imminent cell death.

Before Therapy 4 Days after Therapy

We learn that the chemotherapy is working even BEFORE the tumor cells die.
Living stem cells, labeled with bio-compatible Gadolinium nanoparticles…

tracked *in vivo* using Magnetic Resonance Imaging in a mouse brain as they respond to brain damage resulting from hypoxia.