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## **Introduction to Nuclear Magnetic Resonance Spectroscopy in a Geochemical Setting**

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### Abstract

Nuclear magnetic resonance (NMR) spectroscopy is a powerful analytical tool that is heavily employed in organic chemistry, but lacks use in geochemistry. The technique is most useful for characterization and structural analysis of analytes, but also sees use in kinetics analysis, speciation, and detection. This work aims to answer these questions regarding NMR spectroscopy's use in geochemical settings: Which nuclei are studied? For what purposes is each nucleus studied? What affects the scope of the technique and has caused it to not be widely used? How often is NMR spectroscopy used? What trends are there in the technique's use? The first three questions were investigated with a literature review while the final two questions were investigated with database keyword searches. NMR spectroscopy was found to be used for a variety of analyses of both organic and inorganic earth materials, including but not limited to physical and chemical structure analysis, kinetic analysis of dissolution and other reactions, and characterization. Geochemical use of the technique remains low compared to other techniques due to difficulties with inorganic analytes' sensitivity and decipherability, but recent advances in the past decade have encouraged growth in the use of NMR spectroscopy.

*Keywords:* geochemistry, analytical chemistry, earth science, nuclear magnetic resonance, spectroscopy, chemical structure, speciation

## Introduction to Nuclear Magnetic Resonance Spectroscopy in a Geochemical Setting

Nuclear magnetic resonance (NMR) spectroscopy is an analytical tool that can be used to determine the composition, structure, and connectivity of molecules, allowing for the discerning of an analyte's exact chemical identity.<sup>1,2</sup> While the technique enjoys the most use from organic chemists due to many of the most common organic elements—namely carbon and hydrogen—having isotopes that are well suited for NMR analysis, the technique has also proven invaluable in structural exploration of inorganic materials including those from earth science and geochemistry ever since its invention and early development in the 1940's and 1950's.<sup>1,3,4</sup> The purpose of this study, then, is to study how NMR spectroscopy is used in geochemical settings, including what nuclei are studied and for what purposes, how often NMR spectroscopy is performed, and what affects the technique's scope specifically in the field of geochemistry.

### NMR Spectroscopy

NMR spectroscopy operates on the principle that atomic nuclei have an intrinsic nuclear spin, and nuclei with a non-zero nuclear spin will align their either parallel or antiparallel to an exterior magnetic field (Figure 1). The parallel state is at a lower energy than the antiparallel state, so under normal conditions there are slightly more nuclei in the parallel orientation.<sup>1,2</sup>

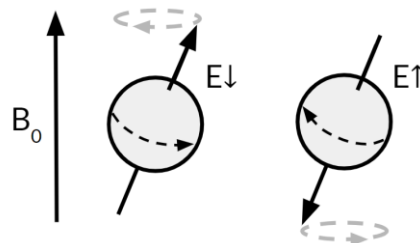
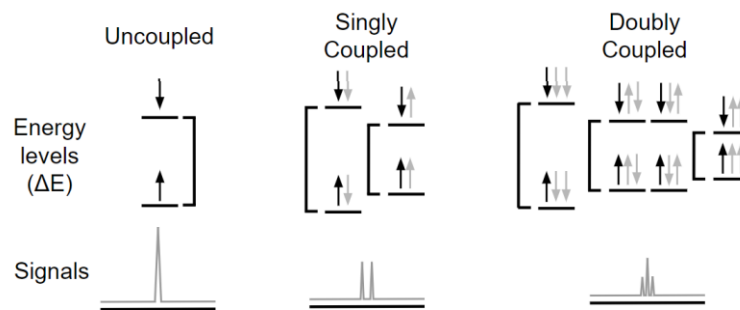


Figure 1 – Spins of low-energy (left) and high-energy (right) nuclei in a magnetic field. Notice that, if not for precession, nuclear spin would be directly parallel with the magnetic field in the low-energy nucleus and antiparallel in the high-energy nucleus.<sup>1,2</sup>

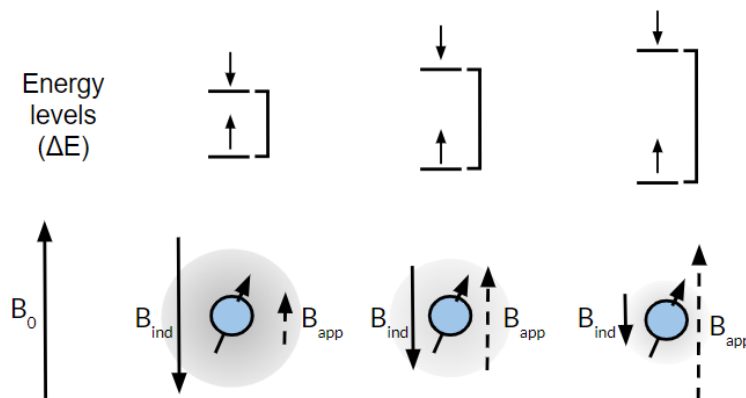
During NMR spectroscopy, a radio frequency resonant with the nuclear spin is pulsed, causing nuclei to re-orientate to the opposite orientation that they were in. As this excited state is not stable, the nuclei quickly relax back to their previous orientations, and in doing so, send out an electromagnetic signal that is received and interpreted as an NMR spectrum. The structural differences between nuclei in distinct parts of a molecule (e.g., for toluene, an aromatic  $^1\text{H}$  versus a methyl  $^1\text{H}$ ) cause nuclei to absorb and emit signal at different frequencies and intensities. By looking at these differences, one can glean information on a molecule's structure, connectivity, and chemical environment.<sup>1</sup> Two key differences that NMR spectroscopy can probe are a nucleus' chemical shift and spin-spin coupling.

Spin-spin coupling occurs when two or more chemically distinct nuclei are near enough to each other in a molecule through bonds to allow one nucleus' spin state to affect the other nucleus' energy level.<sup>1,5</sup> When a nucleus is affected by whether a neighboring nucleus is parallel ("up") or antiparallel ("down"), the signal that it emits is split into two smaller signals (Figure 2). If a nucleus is affected by more than one neighboring nucleus, then the spin-spin coupling stacks and the original signal is further split up into smaller signals. By analyzing the patterns and intensities of these signals, one can obtain a variety of information about a molecule's structure.



*Figure 2 – Energy levels and signals resulting from a nucleus that is uncoupled (left), singly coupled (middle) and doubly coupled to identical nuclei (right). On the right, coupling to two identical nuclei causes four  $\Delta E$ 's to occur, two of which overlap, causing a "triplet" pattern.*

Chemical shift refers to the shift in frequency of a nucleus' signal from that of a reference standard due to its chemical environment—the atoms and electron density physically near to it.<sup>1,2</sup> Nearby electron density has the effect of counteracting the applied magnetic field, effectively shielding a nucleus from some of the field and making it experience an apparent magnetic field less than what is applied (Figure 3). Because the field is weaker, the difference in energy level between the parallel and antiparallel spins is lower, and the nucleus will both absorb and re-emit a signal that is lower in energy (i.e., at a lower frequency). Nuclei whose natural electron density is drawn away by electron withdrawing groups such as carbonyls and halogens will, conversely, lose this protection and are said to be deshielded. This causes a larger difference in energy level between the parallel and antiparallel spin states and a higher frequency signal.



*Figure 3 – Energy levels of nuclei with (left to right) high, moderate, and low local electron density in the presence of a magnetic field  $B_0$ . Note that the more electron density present, the stronger the opposing induced magnetic field,  $B_{ind}$ , and therefore the weaker the apparent magnetic field,  $B_{app}$ , resulting in smaller differences between energy levels.*

In addition to simple addition and subtraction of electron density, chemical shift can also be complicated by the effect that an entire molecule's structure has on the apparent magnetic field, especially in compounds with aromatic groups—exceptionally stable flat cyclic systems whose alternating  $\pi$ -bonds and/or p-orbitals align and allow for their electrons to delocalize—

especially can have a large effect on a nearby nucleus' chemical shift. An applied magnetic field will induce electron movement around the aromatic ring, which creates its own local magnetic field in opposition to the applied field. The combination of these can either shield or deshield a nucleus depending on its position (e.g., a proton on the outside of a benzene ring would be deshielded, causing a higher chemical shift). By analyzing a nucleus' chemical shift, one can obtain much information about its chemical environment, including what functional groups it is attached to or near to, better allowing one to deduce a molecule's full structure.

The scope of NMR spectroscopy is limited by the fact that nuclei must have a non-zero spin to be NMR-active.<sup>1,2</sup> This means that many common isotopes such as  $^{12}\text{C}$ ,  $^{28}\text{Si}$ , and  $^{16}\text{O}$  are unable to be analyzed using NMR spectroscopy because they have a nuclear spin of zero. Further, NMR spectroscopy of nuclei with spins other than  $\frac{1}{2}$  (i.e., those with a quadrupole moment) often becomes more complicated and therefore more difficult to interpret and draw useful conclusions from.<sup>2,4</sup> This means that some isotopes which could be useful to perform NMR spectroscopy on such as  $^{23}\text{Na}$ ,  $^{25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{35}\text{Cl}$ , and  $^{39}\text{K}$  are made more difficult due to broadening of peaks, more peaks from spin-spin coupling, and reduction in signal-to-noise.<sup>4</sup> Now that is not to say that NMR spectroscopy of quadrupolar nuclei is impossible. Some quadrupolar nuclei such as  $^{27}\text{Al}$  are studied relatively frequently due to their high sensitivities and usefulness as analytes outweighing the difficulties in analysis.<sup>4,6</sup> In fact, the quadrupolar and therefore asymmetrical nature of these nuclei can sometimes provide structural information that a dipolar nucleus would not be able to, especially in asymmetrical environments.

## **NMR as a Geochemical Tool**

While NMR is not the most common tool in a typical geochemist's toolbox, it has been used for decades (nearly since its invention) due to many uses in the field and its usefulness in analyzing several different elements of importance.<sup>2,7</sup> Among many,  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  NMR are frequently applied to inorganic materials in geochemistry while  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{31}\text{P}$  NMR are often applied to organic components of rocks and minerals.<sup>2</sup> NMR spectroscopy of  $^1\text{H}$  and  $^{31}\text{P}$  are analyzed below as they both exemplify typical uses of NMR spectroscopy in geochemical settings.

### ***Hydrogen-1***

$^1\text{H}$  is one of if not the most common nucleus analyzed by NMR due to its over 99.9% abundance, nuclear spin of  $\frac{1}{2}$ , and high gyromagnetic ratio, which all combine to make  $^1\text{H}$ -NMR's signal comparatively easy to detect and decode.<sup>1,2</sup> Hydrogen's ubiquity in organic compounds also makes it a universal tool for many different types of organic research and analysis, and its high detectability and decipherability make it a perfect candidate for more complex analysis, such as by two-dimensional NMR or relaxometry.

In the field of geochemistry,  $^1\text{H}$ -NMR has been used for decades (nearly since the invention of NMR itself) to analyze hydrocarbons and other organic compounds in sediment and rocks.<sup>3,7</sup> Such analysis has allowed for exact identification of chemical species present in rock samples, providing insight into the sources and history of organics in those samples. An example of this is found in Chaffee and Fooke's (1988) analysis of hydrocarbons from coal samples.<sup>7</sup> Through  $^1\text{H}$ -NMR spectroscopy, they were able to confirm the suspected structure of many polycyclic hydrocarbons, disprove other suspected structures, and discover unknown



diastereomerism in several of the species present. Through this knowledge, they were able to better understand which hydrocarbons were the source for those in the coal today.

For inorganics,  $^1\text{H}$ -NMR is often used to analyze H-bonding and how  $\text{H}_2\text{O}$  and OH groups are incorporated into crystal lattice structures.<sup>2,8</sup>  $^1\text{H}$ -NMR is regularly used for studies of hydrous materials and hydroxides due to hydrogen's high sensitivity in NMR spectroscopy and low sensitivity in techniques such as X-ray diffraction.  $^1\text{H}$ -NMR can also be combined with other nuclei in coupled or two-dimensional NMR studies to gain information over nuclei which are otherwise difficult to analyze through NMR spectroscopy.

### ***Carbon-13***

Like hydrogen, carbon is present in all organic matter by definition and is therefore a highly valuable analyte for the study of organics.<sup>1,2,3</sup>  $^{12}\text{C}$ , the most abundant stable isotope of carbon, however, has a nuclear spin value of zero and is therefore NMR-inactive. The second-most abundant isotope,  $^{13}\text{C}$ , is NMR-active but suffers from a low natural abundance (less than 1%) and gyromagnetic ratio about a quarter of hydrogen's, which make  $^{13}\text{C}$ -NMR inherently less sensitive and interpretable.  $^{13}\text{C}$ -NMR's utility in understanding organic molecules' structures, however, has meant that  $^{13}\text{C}$  is the second most studied nucleus with NMR spectroscopy. Subsequently,  $^{13}\text{C}$ -NMR has seen much expansion and improvement since its beginnings.

Geochemically,  $^{13}\text{C}$ -NMR is used mainly for analysis of organic portions of sediments and how organic molecules interact with inorganic portions (e.g., adsorption of molecules onto clay minerals).<sup>3,4</sup> The possibilities and scope of organic analysis are robust because of the huge amount of research already done by organic and analytical chemists, meaning most organic molecules can be assigned an exact chemical formula through the use of  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR, even if more advanced techniques such as relaxometry, cross-polarization, or spin echo analysis are

required. When  $^{13}\text{C}$ -NMR cannot (or can but is not used for) provide exact chemical formulas, it can often be used to characterize organic content in soils and sediments. For example, Alekseev and Abakumov (2020) used  $^{13}\text{C}$ -NMR to characterize several different types of Russian tundra soils, analyzing the relative amounts of different types of organic molecules (e.g., aromatic versus aliphatic) by the relative intensities at certain chemical shift bands.<sup>9</sup> This provided insight into the organic matter content and carbon sequestration of permafrost-affected soils as well as information on soil development in such areas.

While carbon is not present in large quantities in many inorganic portions, mainly being confined to carbonates,  $^{13}\text{C}$ -NMR has found use in studying the interactions of  $\text{CO}_2$  with rocks and sediments as well as how it is incorporated into some rocks.<sup>4</sup> For example, Xue et al. (2018) used  $^{13}\text{C}$ -NMR to analyze the structures of silicate glasses (which are amorphous and do not have an organized crystal structure) to determine the speciation of incorporated carbonate.<sup>10</sup> Their study revealed that carbonate prefers to be free in some structures and bonded in other more organized structures. This could help with understanding physical properties of silicate melts that contain dissolved  $\text{CO}_2$ , a subject which could be useful for climatology and geology.

### ***Phosphorus-31***

$^{31}\text{P}$ —while inherently less sensitive than  $^1\text{H}$ —still has a relative detectability about two orders of magnitude greater than  $^{13}\text{C}$  due to its one hundred percent natural abundance, gyromagnetic ratio comparable to  $^{13}\text{C}$ , and spin of  $\frac{1}{2}$ . These all make  $^{31}\text{P}$  NMR reliably achievable and interpretable, even with comparably small amounts of sample.<sup>11</sup> This makes  $^{31}\text{P}$ -NMR especially helpful in analysis of organic components in sediment samples. Assisting geochemists in deciphering the history of organic P in sediments and providing insight into which P-bearing chemical species are present in a sample instead of just giving a total amount of

P present.<sup>11,12</sup> As P is a critical nutrient for life, analyzing the chemical species present can give insight into the life present at certain times in the geological timescale.

One method for analyzing organic P in marine sediment put forward by Defforey et al. (2017) involves first removing all inorganic P.<sup>11</sup> This is extremely important for sediment that has relatively high amounts of inorganic P as it covers signals from organic P, making analysis extremely difficult if not impossible without extremely long runtimes (>24 h) which risk degradation or reaction of analyte. Once inorganic P is removed, including Fe-bound, apatite, and CaCO<sub>3</sub>-bound P, organic P is extracted with an alkaline solution and worked-up for NMR analysis. This method allowed for detection of forms that were previously buried by inorganic P's signal or lost in the background noise, and while the researchers were unable to identify individual peaks from some species such as previous work from other materials such as Turner et al.'s (2003) work with soil samples or Cade-Menun et al.'s (2015) work with bovine feed and feces, the work is promising and shows a bright outlook for the direction of <sup>31</sup>P-NMR analysis of organic P in sediment.<sup>11,13,14</sup>

### ***Silicon-29***

While silicon suffers the same issue as carbon in that the most common stable isotope, <sup>28</sup>Si, is NMR inactive, the second most common isotope, <sup>29</sup>Si, has a nuclear spin of ½ and a natural abundance of 4.7% and gyromagnetic ratio just smaller than <sup>13</sup>C's, making <sup>29</sup>Si-NMR about on the same order of magnitude of detectability and utility as <sup>13</sup>C or <sup>31</sup>P.<sup>3,4</sup> Being one of the most abundant elements in earth materials, silicon is often used for inorganic NMR analysis of silicate structures. Because silicon is mostly found as oxides in the form of silica (SiO<sub>2</sub>) and silicates (SiO<sub>2</sub><sup>4-</sup>) in earth materials, most analysis with <sup>29</sup>Si-NMR focuses on how surrounding cations or silicate structures affect the chemical shifts caused by silicon's covalent bonds to

oxygen. An example of this is how aluminum substitutions for silicon in neighboring silicate tetrahedron cause a predictable chemical shift of +5ppm to the original signal, so by comparing the peaks that are at +5, 10, 15, and 20ppm to the original signal, one can glean the relative amount of aluminum substitution in a sample.<sup>4</sup>

### *Metals*

Metal elements are predictably particularly important parts of geochemical studies as metals make up a large part of inorganic earth materials. Light group one and two cations, period four transition metals, and aluminum play an especially significant role in mineral structure and ecological nutrient cycling.<sup>3,4</sup> Much the same as with <sup>29</sup>Si, many metals' NMR analyses are usually based on chemical shifts changing at predictable intervals. Unlike <sup>29</sup>Si-NMR, however, metal cations' signals mainly change depending on how many anions they are bonded to (i.e., their coordination number) instead of what is bonded to their anions as with <sup>29</sup>Si.

NMR spectroscopy of metals proves a challenge due to many factors. For one, as seen with previous nuclei, many NMR-active metal nuclei have nuclear spins greater than ½, meaning they are quadripolar.<sup>3,4,15</sup> While this is favorable to nuclear spins of zero and being NMR-inactive, their quadripolar nature causes spectra to broaden and exhibit complex behavior, causing issues with interpretation. Further, metal analytes are prone to have unpaired electrons, which was not seen in any of the previously discussed nuclei.<sup>4,15</sup> Electrons also have an intrinsic spin value, so an unpaired electron, like a neighboring NMR-active nucleus, can couple to a target nucleus. Since the distance between an atom's nucleus and electron can proportionally vary much more than the distance between two nuclei, nucleus-electron coupling produces a general broadening affect instead of signal splitting as seen with nucleus-nucleus coupling. This broadening effect can be so severe as to cause a signal to completely fade into the background

noise. These effects, which often occur together, cause many metal nuclei to be extremely difficult to both detect and interpret signals from.

With these challenges in mind, tremendous progress has been made in the realm of NMR spectroscopy of metal nuclei in the past two decades, and especially the past decade.<sup>4,15</sup> While much of this work is carried out by analytical chemists, usually with the aim of analyzing metals interacting in biological contexts, many of the findings are transferable to geochemical contexts, which has allowed for the rapid growth of analysis of nuclei previously too complicated or insensitive to be viable. Recent improvements include those to both hardware and software. Advances in hardware include faster and more refined rotors for Magic Angle Spinning, a method which involves spinning samples at  $54.7^\circ$ , which is the “magic” angle at which several signal-broadening effects reach a minimum and signals for solid state NMR become better resolved. The development of larger, more powerful NMR magnets has also been instrumental in metal nucleus NMR as the difference in energy levels between parallel and antiparallel spin states is directly proportional to the strength of the applied magnetic field. This means that a stronger magnet will result in a stronger, better resolved signal, which is extremely important since many metal nuclei are extremely insensitive analytes. Regarding software, huge advances have been made with advanced pulse sequences, series of electromagnetic pulses applied to the sample and the time in which the desired signal is received. Many of these sequences either make deliberate use of spin-spin coupling or flood a neighboring nucleus with energy to ‘decouple’ it, causing the spin-spin coupling of that neighbor and your target nucleus to disappear. Advanced pulse sequences allow for the decoupling of problematic neighboring nuclei which tend to broaden metal nuclei signals to the point of fading into the background noise.

Some research projects with metal solid state NMR spectroscopy are great examples of how work that is done in a geochemical setting can have far-reaching implications for a variety of fields. For example,  $^{43}\text{Ca}$ -NMR characterization done by Dupree et al. (1997) has been used to explore possible chemical candidates for  $\text{H}_2$  storage, a growing field due to interest in and demand for green energy.<sup>16,17</sup> Similarly, recent research into  $^{27}\text{Al}$ -NMR has provided avenues for fields such as battery development—where aluminum was used to create new high-capacity aluminum-zinc hybrid batteries—and environmental chemical engineering—where aluminum-bearing geopolymers were used to catalyze the degradation of a pollutant.<sup>6,18,19</sup>

### Frequency of Use

To see the relative frequency of use of NMR spectroscopy as compared to other geochemical techniques that can be used to determine composition and/or structure of earth materials, a keyword search was performed on GeoRef—a geological database of published journal articles, American and Canadian graduate school theses and dissertations, and USGS publications—and the number of results per year was recorded (Figure 4, full data appended at end). Given the lag between technique use, article publication, and database aggregation, results from 2023 and 2024 were not used for analysis. Only results from peer-reviewed sources were counted. Techniques studied were (in order of popularity): x-ray diffraction (XRD), x-ray fluorescence (XRF), mass spectrometry (MS), infrared (IR) spectroscopy, NMR spectroscopy, and inductively coupled plasma optical emission spectroscopy (ICP-OES). Keywords (listed in the legend of Figs 4 and 5) were chosen to maximize the results of each technique (e.g., “nuclear magnetic resonance” consistently had more results than “nmr spectroscopy”). For ICP-OES, the keyword chosen was “OES” as it maximized results while minimizing false positives from the

similarly named inductively coupled plasma mass spectrometry (ICP-MS). The first twenty results for each technique from each decade were checked for false positives to ensure consistency and accuracy.

The results show a gradual increase in NMR spectroscopy use throughout the years analyzed, which mirrors the rises seen in other techniques. NMR spectroscopy's use is seen to be increasing steadily, growing at approximately five more articles yearly from 2003 to 2019 before outshooting expected growth in 2020 with sixty-four more articles than in 2019. This has resulted in NMR spectroscopy having over 200 individual search results per year for the past three years analyzed (2020-2022). Figure 5 shows that NMR spectroscopy is not as highly utilized as common techniques such as MS, XRD, and XRF—generally staying around a quarter of the results of MS and XRF for the entire time analyzed and around a tenth of the results of XRD in the past three decades. NMR spectroscopy is seen, however, to keep pace with other geochemical techniques such as IR spectroscopy and ICP-OES.

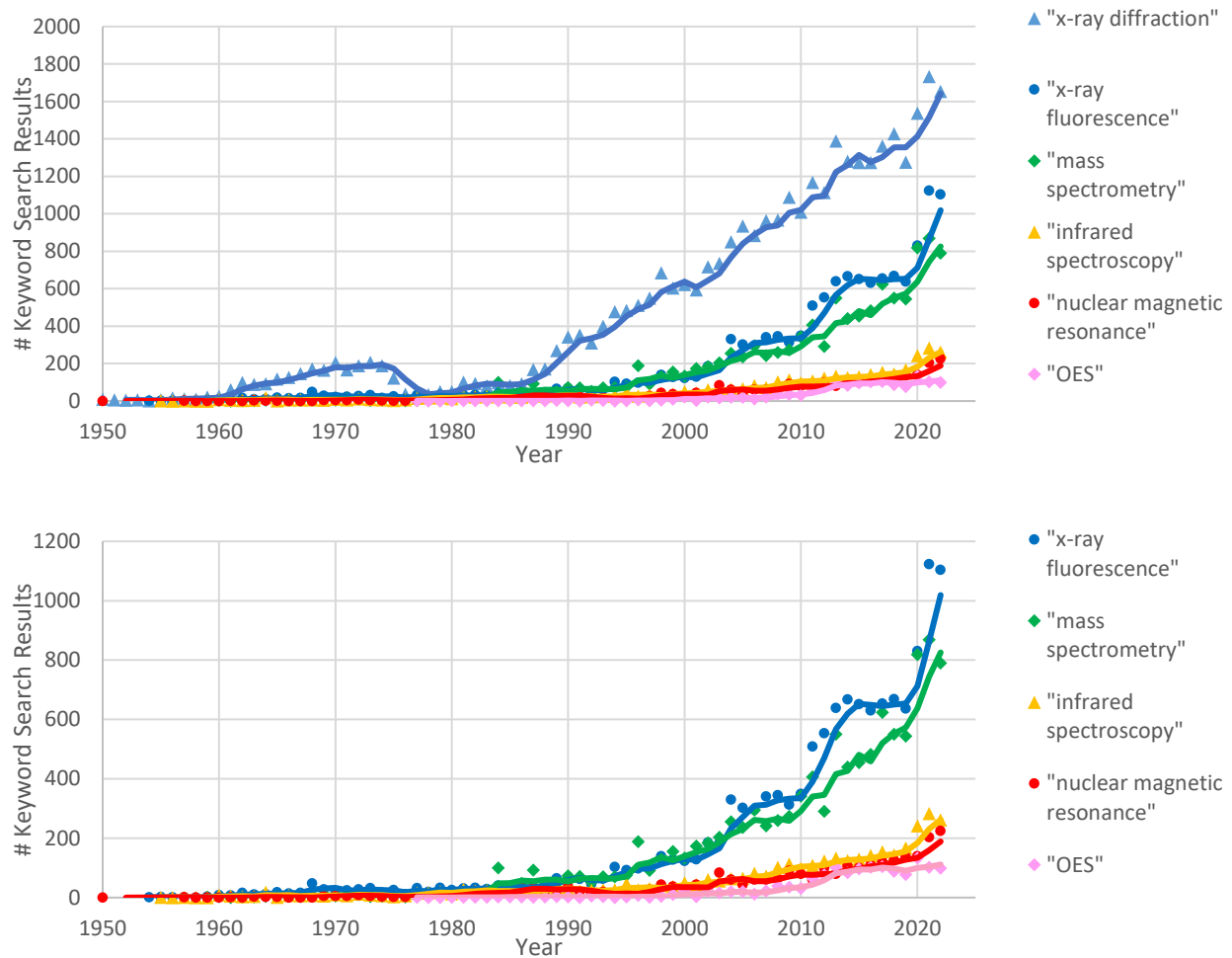


Figure 4 – Number of GeoRef keyword results for select geochemical techniques from 1950-2022. The bottom graph excludes data for XRD to show less frequently used techniques better. Trendlines are 3-year moving averages.

A shortcoming of this method was seen in that, while able to show the absolute popularity of each technique, it did not account for the growth of geochemistry as an entire field nor the general increase in sources for GeoRef to draw from (e.g., an increasing number of international journals became available throughout the time analyzed). To account for this, another search was performed for the keyword “geochemistry” with all the same parameters in hopes that this would serve as a standard for the popularity of geochemistry as a field. Yearly results for technique searches were then divided by the corresponding year’s “geochemistry” result (Figure 5). This



provides an estimation of the percentage of geochemistry publications each year that made use of a given technique. This highlights NMR spectroscopy’s newfound increase in popularity in the past four years

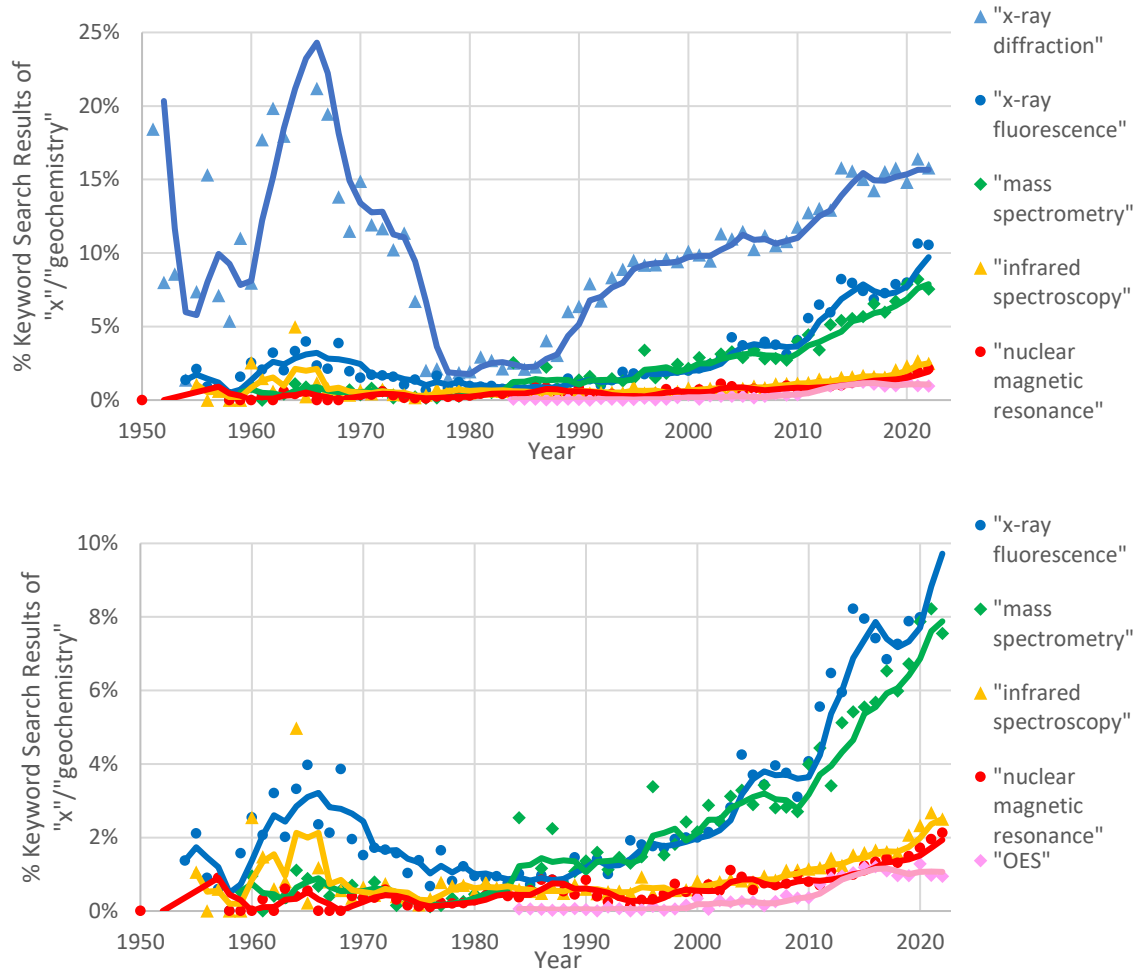


Figure 5 – Number of GeoRef keyword results for select geochemical techniques from 1950-2022 divided by the keyword results for “geochemistry”. The bottom graph excludes data for XRD to show less frequently used techniques better. Trendlines are 3-year moving averages.

One limiting factor that could be suppressing the use of NMR spectroscopy is the relatively prohibitive cost of NMR spectrometers compared to that of other instruments. This means that only schools and research institutions that can both cover and justify the cost of the instrument will end up having one. Since the scope of NMR spectroscopy is much more geared

towards organic chemistry, it is much more likely that an academic institution or a company that researches organic molecules like in pharmaceuticals would have an NMR spectrometer than many geology or environmental labs.

## **Conclusion**

While NMR spectroscopy is by no means the most common technique used in a geochemical setting, it still plays an important role in geochemistry and can be used for a variety of purposes such as discerning chemical and physical structures, studying dissolution and kinetics of reactions, and characterizing species found in rocks, sediments, and soils. NMR spectroscopy is still clearly used more for analysis of organic material as it has historically been closely tied to organic chemistry and is most suitable for analytes like  $^1\text{H}$  and  $^{13}\text{C}$  which are ubiquitous in organic compounds, but it has been used in many inorganic applications. In fact, the potential of inorganic NMR analysis will only grow as recent advancements alleviate the issues seen with metal nuclei NMR spectroscopy, and the beginnings of that rise can already be seen in the increase in NMR GeoRef keyword search results from the past decade. As new improvements are made to the hardware and programming of NMR as well as in advanced techniques such as relaxometry, study of anisotropic effects, and two-dimensional NMR, we will no doubt see a rise in geochemical NMR spectroscopy, and from that, new avenues of research for both researchers in fields like ecology, materials science, and engineering as well as geochemists themselves.

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## Appendix

Year	NMR	MS	XRF	IR	XRD	ICP-OES	"geochemistry"
1950	0	0	0	0	9	0	26
1951	0	0	0	0	7	0	38
1952	0	0	0	0	4	0	50
1953	0	0	0	0	6	0	70
1954	0	0	1	0	1	0	73
1955	0	0	2	1	7	0	95
1956	1	0	1	0	17	0	111
1957	0	0	1	1	12	0	169
1958	0	0	0	0	10	0	186
1959	0	1	3	0	21	0	191
1960	1	3	8	8	25	0	314
1961	0	0	7	5	60	0	339
1962	3	2	16	3	99	0	499
1963	2	2	10	4	89	0	496
1964	2	4	12	18	93	0	362
1965	0	4	18	1	118	0	453
1966	0	4	14	7	126	0	595
1967	0	3	16	6	146	0	751
1968	5	7	48	7	172	0	1245
1969	5	10	28	5	165	0	1437
1970	5	5	21	9	206	0	1384
1971	8	11	24	6	166	0	1394
1972	5	10	27	12	189	0	1621
1973	3	3	32	8	208	0	2036
1974	2	4	17	6	188	0	1657
1975	2	4	25	3	122	0	1816
1976	4	2	12	6	36	0	1782
1977	4	3	32	15	41	1	1937
1978	5	8	19	16	35	0	2342
1979	8	7	33	19	51	0	2726
1980	11	12	25	13	51	1	2630
1981	19	23	31	27	101	1	3438
1982	14	18	33	22	94	1	3496
1983	14	24	29	23	81	1	3829
1984	22	100	40	23	99	2	3945
1985	33	24	28	21	82	2	3911
1986	35	48	40	20	93	2	4142
1987	22	93	35	27	168	1	4148
1988	25	42	45	27	172	2	5643
1989	38	48	65	32	269	3	4465

<b>Year</b>	<b>NMR</b>	<b>MS</b>	<b>XRF</b>	<b>IR</b>	<b>XRD</b>	<b>ICP-OES</b>	<b>"geochemistry"</b>
<b>1990</b>	21	73	69	32	342	2	5365
<b>1991</b>	11	71	63	21	353	0	4456
<b>1992</b>	19	52	46	24	310	5	4603
<b>1993</b>	7	70	64	26	400	3	4801
<b>1994</b>	16	70	103	26	478	0	5376
<b>1995</b>	16	75	92	47	484	2	5091
<b>1996</b>	26	188	98	26	511	7	5566
<b>1997</b>	44	91	102	31	549	1	5965
<b>1998</b>	37	129	139	40	685	4	7121
<b>1999</b>	25	155	128	37	603	10	6407
<b>2000</b>	44	133	123	50	623	21	6168
<b>2001</b>	33	173	129	43	594	3	6011
<b>2002</b>	84	184	185	60	717	21	7582
<b>2003</b>	60	203	183	56	735	16	6502
<b>2004</b>	44	255	330	64	850	20	7763
<b>2005</b>	61	236	302	65	935	20	8152
<b>2006</b>	60	295	296	82	884	12	8627
<b>2007</b>	64	242	341	72	964	22	8625
<b>2008</b>	90	260	345	102	966	39	9199
<b>2009</b>	80	273	313	113	1089	35	10096
<b>2010</b>	60	342	349	98	1009	31	8573
<b>2011</b>	99	406	509	108	1167	66	9157
<b>2012</b>	80	291	553	123	1113	77	8548
<b>2013</b>	106	550	639	133	1388	102	10743
<b>2014</b>	100	440	667	124	1281	84	8118
<b>2015</b>	109	454	651	130	1274	97	8186
<b>2016</b>	121	482	630	141	1274	102	8494
<b>2017</b>	125	624	654	154	1361	104	9554
<b>2018</b>	137	550	668	144	1428	88	9195
<b>2019</b>	139	544	637	167	1275	78	8088
<b>2020</b>	203	818	830	242	1538	133	10391
<b>2021</b>	225	869	1123	283	1733	102	10568
<b>2022</b>	237	790	1104	262	1654	99	10470
<b>2023</b>	159	615	683	138	966	66	6655
<b>2024</b>	14	68	81	6	100	3	666