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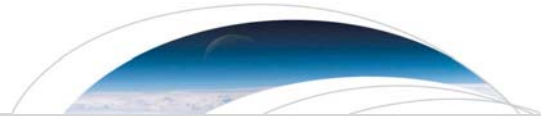
Lehmann-Horn, J. A, Miljak, D. G, O'Dell, L. A, Yong, R. and Bastow, T. J. 2014, Rapid detection of arsenic minerals using portable broadband NQR, *Geophysical Research Letters*, vol. 41, no. 19, pp. 6765-6771.

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RESEARCH LETTER

10.1002/2014GL061386

Key Points:

- Transformation of chemical analysis method to geophysical detection technology
- First NQR ore characterization of selected arsenic minerals in bulk volumes
- Broadband NQR sensor to detect arsenic minerals with low crystallinity

Supporting Information:

- Readme
- Figures S1–S4

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Citation:

Lehmann-Horn, J. A., D. G. Miljak, L. A. O'Dell, R. Yong, and T. J. Bastow (2014), Rapid detection of arsenic minerals using portable broadband NQR, *Geophys. Res. Lett.*, 41, 6765–6771, doi:10.1002/2014GL061386.

Received 29 JUL 2014

Accepted 26 AUG 2014

Accepted article online 28 AUG 2014

Published online 13 OCT 2014

Rapid detection of arsenic minerals using portable broadband NQR

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Abstract The remote real-time detection of specific arsenic species would significantly benefit in minerals processing to mitigate the release of arsenic into aquatic environments and aid in selective mining. At present, there are no technologies available to detect arsenic minerals in bulk volumes outside of laboratories. Here we report on the first room-temperature broadband ⁷⁵As nuclear quadrupole resonance (NQR) detection of common and abundant arsenic ores in the Earth crust using a large sample (0.78 L) volume prototype sensor. Broadband excitation aids in detection of natural minerals with low crystallinity. We briefly discuss how the proposed NQR detector could be employed in mining operations.

1. Introduction

Nuclear quadrupole resonance (NQR) is a radio frequency (RF) spectroscopy to detect pharmaceuticals, explosives, and other solid materials containing nuclei with nonzero quadrupole moment [Das and Hahn, 1958; Suits, 2006; Harbison, 2012; Balchin et al., 2005]. The method is closely related to nuclear magnetic resonance (NMR) but operates without an external static magnetic field. It foregoes the (superconducting) magnet which makes the sensor more portable, less expensive, and potentially applicable in remote locations. Portable NQR sensors have been used in the past to detect land mines [Carroway et al., 2001]. However, until now, it has not been used as a geophysical measurement method to determine mineralogy in geophysical field studies.

In contrast, NMR is widely used in geophysical applications to analyze porous rocks which carry a significant amount of petroleum, gas, and water. A variety of field applications in low fields including well logging [Kenyon, 1992] and groundwater exploration [Lehmann-Horn et al., 2011; Grunewald and Walsh, 2013] are well known. Geophysical NMR investigations of nuclei other than ¹H are rare due to the lower sensitivity. Larger sensitivities can be achieved in solid state NMR devices which operate at high fields (9–23.5 T). However, it remains difficult to create high fields outside of laboratories such as in single-sided or borehole sensors. Even in solid state NMR laboratories, ⁷⁵As studies are uncommon due to the strong quadrupolar interaction and low-coordination symmetry in many compounds. The large quadrupolar moment of ⁷⁵As and its noncubic coordination in many crystals lead to very broad NMR powder line widths [Bowers and Kirkpatrick, 2007] and make measurements extremely challenging. Conversely, NQR may sometimes be readily observable and NQR lines have been reported for many common arsenic minerals such as arsenopyrite (FeAsS), domeykite (Cu₃As), enargite (Cu₃AsS₄), lautite (CuAsS), lollingite (FeAs₂), niccolite (NiAs), orpiment (As₂S₃), proustite (Ag₃AsS₃), realgar (As₄S₄), and tennantite (Cu₁₂As₄S₁₃) [Lehmann-Horn et al., 2013; Bastow and Whitfield, 1981]. The ⁷⁵As and ⁶³Cu NQR absorption lines of common arsenic minerals are summarized in Figure 1a.

The major arsenic minerals occurring in nature are summarized in the work of Smedley and Kinniburgh [2002], which includes, for example, FeAsS, As₂S₃, and As₄S₄. These minerals have been identified as an important source and cause of arsenic contaminations in groundwater aquifers [Harvey et al., 2002; Fendorf et al., 2010]. Concentrations above 50 μg/L have been identified in various parts of the world [Williams, 2001]. Exposure of arsenic rich waters has serious health effects, and its negative consequences can be observed in regions such as Bangladesh and Argentina [Smedley and Kinniburgh, 2002].

Arsenic minerals occur prominently in certain types of gold, copper, and nickel deposits. Gold in particular can be intimately associated with specific minerals such as FeAsS, FeAs₂, and arsenian pyrite (Fe(As,S)₂) [Arehart et al., 1993; Moller and Kersten, 1994; Palenik et al., 2004; Smon et al., 1999]. In copper deposits where arsenic is significant, the arsenic containing minerals Cu₃AsS₄ and Cu₁₂As₄S₁₃ may in fact carry a significant

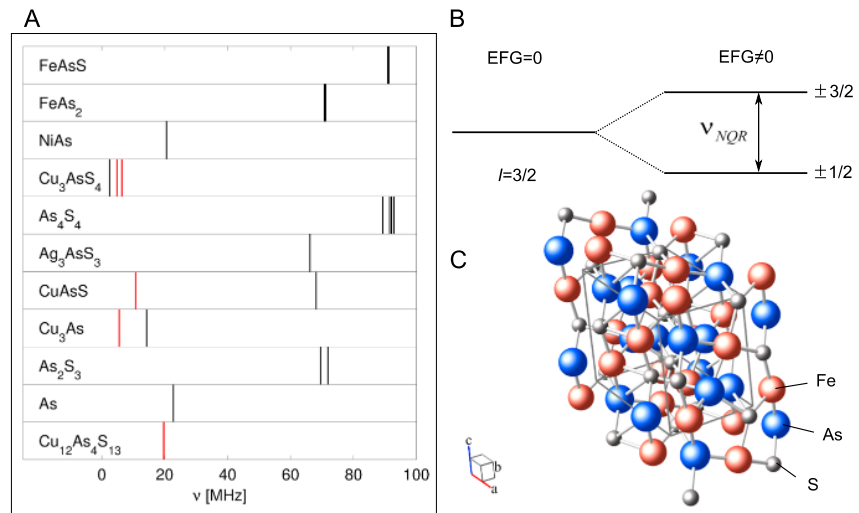


Figure 1. (a) Graphical overview of ⁷⁵As (black lines) and ⁶³Cu (red lines) NQR absorption lines of selected arsenic minerals. Frequencies have previously been determined from high-field NMR measurements, density functional theory simulations, and zero-field sweeps [Lehmann-Horn et al., 2013; Bastow and Whitfield, 1981]. (b) Nuclear spin $I=3/2$ energy levels due to an electric field gradient (EFG) with its corresponding transition frequency ν_{NQR} and (c) crystal structure (monoclinic) of FeAsS

fraction of the economically important copper. In some deposits arsenic itself is extracted because of its value to the semiconductor industry [Yoon et al., 2010]. Despite the value associated with some arsenic minerals, the presence of arsenic in ore streams remains problematic from both an economic and environmental point of view. The exploitation of these deposits has been identified in some cases as an important cause of arsenic contaminations of mine water, surface drainage, and groundwater aquifers. Imperfect mineral processing may lead to excessive arsenic levels in mineral concentrates that incur an economic penalty to the concentrate producer. The timely detection of specific arsenic species on site would help to mitigate the release of arsenic into mine waters. In addition, the real-time characterization of arsenic mineral phases in bulk volumes would benefit both selective mining and mineral processing, by enabling ore sorting or advanced mineral flotation control [Ma and Bruckard, 2009].

In this letter, we report on the first broadband ⁷⁵As NQR measurements of FeAsS, As₂S₃, As₄S₄, and FeAs₂ in bulk volumes. Frequency-swept pulse sequences are employed to excite absorption lines of natural arsenic minerals which are broadened due to crystalline disorder. The large-volume NQR sensor is described, and a brief discussion is provided on how the proposed technology may be employed for bulk mineral analysis in geophysical mining operations.

2. NQR Theory

Quadrupolar nuclei have spin $I > 1/2$ and have a nonzero quadrupole moment, which will couple to a local electric field gradient (EFG) generated by the surrounding electron clouds [Das and Hahn, 1958; Man, 2011]. This quadrupolar interaction gives rise to quantized energy levels and one or more observable transitions even in the absence of an external magnetic field (Figure 1b). For spin $I=3/2$ nuclei such as ⁷⁵As and ⁶³Cu, a single nuclear quadrupole resonance transition occurs at a frequency ν_{NQR} given by

$$\nu_{NQR} = \frac{1}{4} \frac{C_Q}{2} \left(1 + \frac{\eta^2}{3} \right) \quad (1)$$

In this expression, C_Q and η are parameters that describe the EFG tensor and are defined via its principal components $|V_{33}| \geq |V_{22}| \geq |V_{11}|$. The quantity C_Q is known as the quadrupolar coupling constant and is equal to eQV_{33}/h where eQ is the nuclear quadrupole moment and h is the Planck's constant. The asymmetry parameter η is equal to $(V_{11} - V_{22})/V_{33}$ and varies between 0 and 1. These parameters are highly sensitive to the structural environment surrounding the nucleus (i.e., the crystal structure, Figure 1c), and the NQR

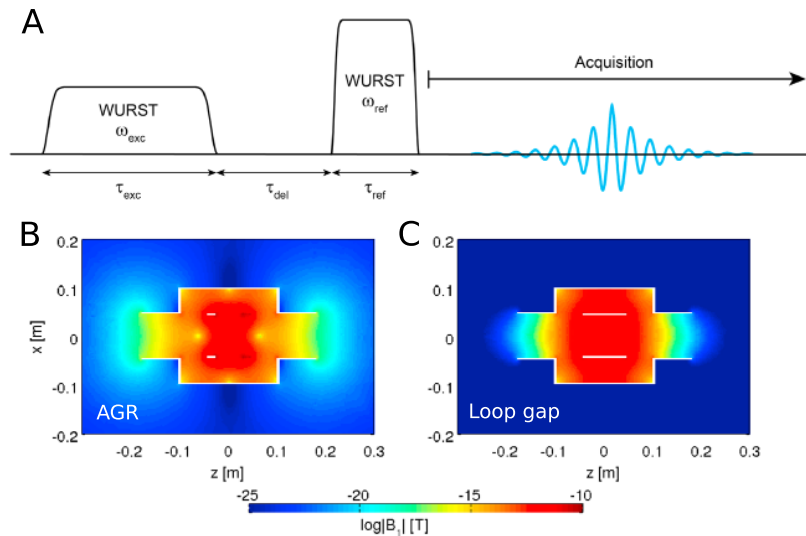


Figure 2. (a) The WURST spin echo pulse sequence, with pulse durations $\tau_{exc,ref}$ and the delay between the two pulses τ_{del} . Total RF magnetic field B_1 distribution (at unit current) at $\nu = 70$ MHz for a partly shielded (b) AGR and (c) loop-gap coil.

frequency thereby provides a fingerprint for the crystallographic site observed. For ^{75}As , typical values for C_Q are 120–180 MHz and the NQR frequencies therefore span a range of approximately 60–90 MHz. To observe the NQR transitions a standard NQR experimental measurement sequence involves applying a radiofrequency excitation pulse of duration τ_{exc} to the sample, a pulse delay time τ_{del} and application of a second refocusing pulse of duration τ_{ref} . After the second pulse, the spin echo is recorded and transformed into the frequency domain using a conventional fast Fourier transform.

3. Broadband Excitation

In this work, we have used specialized excitation and refocusing RF pulse shapes called WURST (wideband, uniform rate, and smooth truncation) pulses [Kupce and Freeman, 1996]. The phase ϕ of a WURST pulse (in radians) is modulated as a quadratic function of time:

$$\phi \propto \frac{1}{4} \pm 2\pi \frac{\Delta}{2} t \pm \frac{\Delta}{2T} t^2 \quad (2)$$

This modulation results in a linear sweep of the pulse's effective frequency across an arbitrary frequency range Δ over its duration τ (see Figure 2a). Such pulses were originally developed as broadband adiabatic inversion pulses for NMR spectroscopy [Kupce and Freeman, 1996] but have more recently found a diverse range of applications in broadband excitation and refocusing in both NMR and NQR [O'Dell, 2013]. When used as excitation pulses in the nonadiabatic regime, they can excite frequency ranges of up to several hundred kHz, far exceeding the bandwidths of standard, fixed-frequency RF pulses. This large bandwidth makes WURST pulses extremely useful in NQR applications, and for this work in particular they bring another important advantage which is that their optimum RF power can be considerably lower than that of standard RF pulses (see supporting information). For large sample volumes, the RF coil dimensions impose severe limitations on the strength of the RF magnetic field B_1 , so standard excitation pulses must have long durations and correspondingly narrow bandwidths. Due to their phase modulation, WURST pulses are exempt from this "duration $\tau \times$ bandwidth $\Delta \approx 1$ " limitation.

4. The NQR Sensor

Most geophysical experiments are performed outside of laboratories; therefore, simple and robust instrumentation is crucial. These requirements are fulfilled by NQR systems. A basic NQR sensor is composed of the following electronic parts: RF transceiver coil, tuning-matching circuit, power amplifier, switches, and receiver electronics [Suits, 2006]. Compared to high-field NMR laboratory instruments (which are based on

superconducting magnets, nitrogen cooling, and shimming electronics) the NQR measurement setup is straightforward and can be designed in a compact and portable manner. We have designed a NQR prototype sensor with a sample volume of 0.78 L. A loop-gap coil or an Alderman-Grant resonator (AGR) [Mispelter et al., 2009] can be used as transceiver coil (RF coil in Figure 4). A symmetric tuning-matching circuit has been applied to balance the coil [Mispelter et al., 2009] and match the system to 50 Ω for optimal power transfer. The resonator was driven by a 2 kW class AB power amplifier (Tomco Technologies).

The electromagnetic skin depth in typical rocks and crushed ores at NQR frequencies discussed in this study spans 0.2 m to greater than 1 m, depending on the rock conductivity. Therefore, the rock size is not a particular limitation on the application of NQR. The skin depth within individual semiconducting mineral grains is somewhat smaller but does not limit applications involving dispersed mineralization that characterize, for example, many porphyry deposits. The large rock skin depth and consequent possibility for sampling large ore volumes is a major advantage compared to other material characterization technologies.

A limitation of many RF spectroscopy methods is its low signal-to-noise ratio (SNR), especially, when the sensor is exposed to external noise sources. External electromagnetic noise in an "open" NQR sensor, where the sensor cannot entirely be shielded from its surrounding, can be a major challenge outside of laboratories. The noise induced in NQR sensors by external fields can be estimated using the principle of reciprocity [Hoult, 2000]. Computation of the RF field distribution generated by sensors at distances outside the sensor volume can be used to infer susceptibility to external electromagnetic noise sources at these distances. Figures 2b and 2c show a comparison of the magnetic field distribution between the loop gap coil and the AGR resonator, where lower magnetic field strength outside of the sensor is indicated for the loop gap coil. The distributions were computed using a commercially available simulation package (Comsol Multiphysics). Eddy currents induced in the open ends of the shield are stronger in the case of the AGR resonator. Therefore, the AGR coil is more susceptible to external noise sources under conditions discussed here.

NQR spin-spin resonance relaxation times T_2 are typically in the order of 100–1000 μ s for diamagnetic materials. In the case of long T_2 spin-spin resonance relaxation times ($> 200 \mu$ s), longer RF pulse durations (to reduce the peak power of power amplifier) and longer delay times (to reduce echo interference with probe ring down) can be employed without losing SNR. The bandwidth is independently controlled due to the WURST pulse sequences. By applying weak external magnetic fields (1–50 mT) to natural FeAsS and FeAs₂ samples, an increase in T_2 relaxation times by up to a factor of 5 has been detected. Weber and Hahn [1960] reported that spin-spin transition probabilities can be reduced in NQR by applying weak static external magnetic fields. Detailed experimental results on T_2 dependence with weak external fields will be discussed elsewhere. In the presence of the weak field (applied in our studies with a Helmholtz coil configuration) we used an AGR resonator to minimize the geometrical mutual coupling between the DC and RF coils. Site and material specific conditions have to be taken into account prior to sensor installation, and other resonators might be preferred. All of the following experiments were performed with an AGR.

5. Experimental Results

Our ⁷⁵As NQR study covers the natural minerals FeAsS, FeAs₂, As₂S₃, and As₄S₄. As₂S₃ has two narrow NQR lines at 69.54 and 71.94 MHz, corresponding to two As sites. The high-frequency line is close to the response of FeAs₂ which is located at 71.05 MHz. The zero-field resonance of As₄S₄ is represented by four sharp lines between 88 and 92 MHz which occupy narrow regions within the wide-NQR spectrum of FeAsS as shown in Figure 1a. All samples discussed in this study were ground into coarse powders (millimeter-sized grains). X-ray diffraction (see supporting information) and chemical analysis of the samples confirmed high phase purity in each case. The NQR measurements were recorded on our large-volume prototype spectrometer discussed in section 4. Measurements for FeAsS were conducted in the presence of a weak (inhomogeneous) static magnetic field of 2 mT.

All spectra in Figure 3 were recorded at room temperature using a WURST spin echo pulse sequence: $\tau_{exc} \square \tau_{del} \square \tau_{ref}$ as shown in Figure 2a. Typical pulse widths of $\tau_{exc} = 100 \mu$ s and $\tau_{ref} = 50 \mu$ s with a pulse delay of $\tau_{del} = 100 \mu$ s to 175 μ s were employed. The RF amplitude were set to $\omega_{ref} = 3\omega_{exc}$, and the bandwidth is $\Delta = 50$ kHz. The repetition rate was typically set to 100 ms, the quality factor of the coil was about 400 for all measurements. The number of scans was set to 2000 for FeAs₂, As₂S₃, As₄S₄, and 10000 for FeAsS. Relaxation

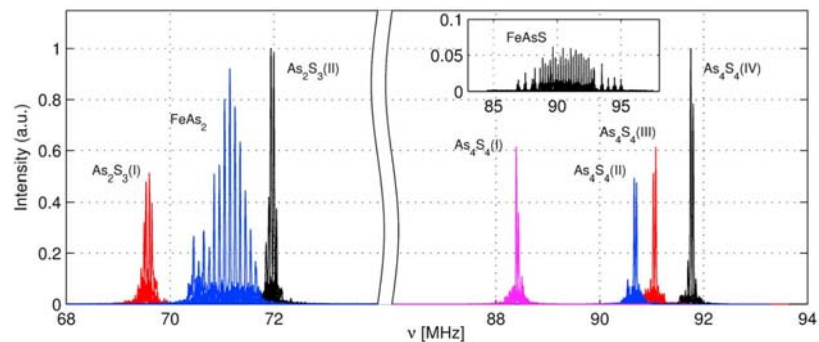


Figure 3. Broadband NQR spectra (normalized intensity) of the arsenic minerals (left) FeAs_2 and As_2S_3 and (right) FeAsS and As_4S_4 . The spectra were recorded with the WURST pulse sequence as shown in Figure 2 with the pulse parameters $\tau_{\text{exc}} = 100 \mu\text{s}$, $\tau_{\text{del}} = 100 \mu\text{s}$ to $175 \mu\text{s}$, $\tau_{\text{ref}} = 50 \mu\text{s}$, $\omega_{\text{ref}} = 3\omega_{\text{exc}}$, and a bandwidth of $\Delta = 50 \text{ kHz}$ and frequency hopping of 50–100 kHz.

times were determined for all specimens to ensure the resulting line shapes were not distorted. The signal-to-noise ratio was 7.5 for As_2S_3 at 71.96 MHz. The peak RF power was 2 kW, which corresponded to an average power of about 0.6 W for the pulse sequence used. The peak power was set so as to approximately maximize signal-to-noise ratio obtained using the chosen pulse sequence. An exhaustive study of power, probe quality factor, and pulse sequence trade-offs has not been completed here, and it is conceivable that a different pulse width and power combination could result in improved overall performance. It is noted however that both the peak and average power parameters employed in this study are simultaneously within reach of miniaturized and portable systems, such as those demonstrated in prototype systems for NQR explosives detection.

The spectra were collected by a combination of wideband pulse sequences and frequency stepping. Each line has a width of 50 kHz, and reference frequency is manually shifted by 50 or 100 kHz after each acquisition. In the future, the whole spectrum can be recorded by a combination of several channels. Each channel operates over a selected bandwidth by stepping the reference frequency using an automatic impedance tuning-matching circuit and applying wideband pulses to select a user-defined bandwidth and bypass the “ $\tau \times \Delta \approx 1$ ” limitation.

This initial study has demonstrated the possibility to obtain a large signal-to-noise ratio in a short acquisition time. The 3σ detection limit (expressed as the percentage weight of arsenic) over a 60 s acquisition period was determined as 0.25 wt % for FeAs_2 and 0.08 wt % for As_2S_3 and As_4S_4 . Due to its lower sensitivity, the detection limit for FeAsS was determined over a 20 min acquisition period as 1.23 wt %. In computing the concentration limits (see supporting information), an average ore bulk density of 1.6 kg/L was assumed within the coil volume of 0.78 L, and in each case the instrument detection bandwidth was 60 kHz. These initial sensitivities are encouraging, and in future significant optimization can occur toward improving detection limits, especially with regard to optimal pulse repetition rate and further increases in sample volume.

6. Discussion

Our experiments showed that selected arsenic phases can be detected and monitored in bulk volumes using the NQR technology. Broadband excitation pulses helped to characterize minerals with low crystallinity. The minerals studied here occur in a variety of settings including certain types of gold and base metal mineral deposits. The NQR sensor is not limited to ^{75}As materials detection but can be adapted for solids containing ^{63}Cu , ^{123}Sb , and ^{209}Bi measurements (to name only a few). Core sampling or online based NQR sensors could help to identify ore zones rich in arsenic during exploration and mining in the future. Selected arsenic phases could be selectively removed from the process stream before grinding. Later in the processing chain, the selective flotation of arsenic phases could be optimally controlled with knowledge of the arsenic phase mixture, avoiding arsenic entrainment in concentrates that are subsequently smelted. The smelting of arsenic containing ores is a significant known channel for environmental arsenic release.

A future large-volume NQR sensor to detect selected arsenic minerals in the processing stream might be implemented as shown in Figure 4. The crushed rocks pass on a conveyor belt (or in a slurry pipe) through the resonator. The selected arsenic mineral content in the ore stream can be estimated by the NQR signal

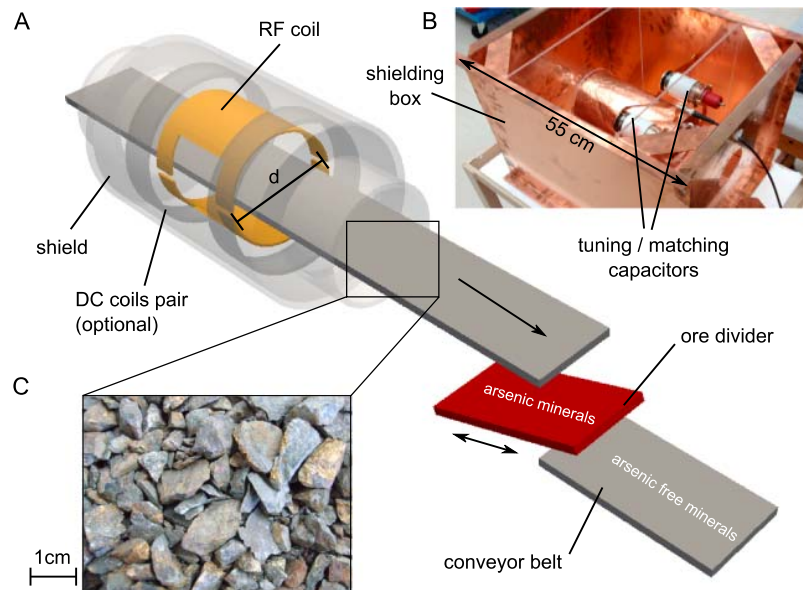


Figure 4. (a) Large-volume NQR sensor for arsenic phase detection: crushed ore minerals pass on a conveyor belt through the shielded resonator (RF coil). An optional static magnetic field is applied by a Helmholtz coils pair (DC coils). The selected arsenic mineral content in the ore stream can be estimated by the NQR signal strength and simultaneous density measurements. The NQR sensor controls the ore divider to separate the arsenic minerals from the processing stream. The RF coil diameter d may vary between $d = 0.1$ and 1.0 m with respect to its application (exploration, mining, and conveying). Photography of (b) the prototype detector and (c) natural ore samples.

strength and simultaneous mass loading measurements. The sensor controls the “ore divider” to separate the arsenic phase from the processing stream.

In case of conveying, the relevant belt feed rate for large base metal mines is in the order of 2000 t/h or less for partial streams. This corresponds to lots of approximately 30 t in a minute, a relatively small amount for these operations where minimum mining units are often tens of thousands of tons. Measurement lots for nuclear magnetic resonance or nuclear quadrupole resonance based sorting are therefore well below mining resolution and likely to see significant variation due to the persistent nature of grade variation (see McGraw [2013] for variation in copper porphyry deposits), therefore making sorting on minute time scales potentially useful. The value of NQR measurements in this context can be seen in the following.

First, in many deposits arsenic phases are associated with gold and other precious metals, and their presence could act as a metal proxy. Their rapid detection (on a minute time scale as demonstrated in this study) during exploration, mining, or conveying to stockpile would allow significant opportunities to selectively raise the feed material grade and provide step change reductions in the energy and water use footprint of mineral processing. The upgrade could occur by actively sorting gangue material from a primary ore stream or selectively stockpiling larger lower-grade ore parcels early in the mining process.

Second, in cases where the arsenic is a major penalty element, the ore zones rich in arsenic could be selectively removed from the process stream before grinding. In mineral flotation, the problematic arsenic phases could be selectively separated, avoiding arsenic entrainment in concentrates that are subsequently smelted. The smelting of arsenic containing ores is a significant known channel for environmental arsenic release. The detection of selected arsenic phases would help to diminish the release of arsenic into mine waters. The phase of the arsenic bearing minerals in exploration, sorting, and process control applications is arguably just as important as the level of arsenic itself. In this regard, NQR potentially provides a unique phase measurement solution in geophysical and minerals processing applications for large volumes of primary material.

The wide range of NQR absorption lines for the most prominent arsenic mineral as shown in Figure 1 allow a maximal discrimination so that there are only small resonance frequency overlaps. The detection is essentially interference free, with only spectrometer and environmental noise determining the detection limit for a given mineral. This is a useful feature from the point of view of performing robust multiphase

discrimination in mineral ores. Accuracy of arsenic mineral concentration measurement may be affected by variations in relaxation times and line width. However, our broadband system can account for line width variations. Relaxation time variability, if occurring within deposits, may in principle be also measured with further modification of pulse sequences. The variability of relaxation times could be considered as an additional source of information with regard to crystal perfection and impurities.

7. Conclusions

We have shown that NQR can be extended from a chemical analysis method in laboratories to a large-volume geophysical sensing tool to characterize mineralogy. The detection of broadband NQR arsenic mineral resonances using a large-volume sensor has been reported for the first time. This significant improvement in NQR technology will help to selectively detect and separate problematic arsenic phases during exploration, mining, and conveying. It is hoped that this successful demonstration of rapid broadband arsenic minerals detection will encourage the development of large-scale sensors helping to mitigate the release of arsenic into mine waters and reduce the energy and water usage in mineral processing.

Acknowledgments

Data for this paper are available for free upon request via email to either J.L.H. (jochen.lehmann-horn@siro.au) or R.Y. (richard.yong@siro.au). J.L.H. was supported by the capability development fund within the Postdoctoral Fellowship Program of CSIRO. T.J.B. is grateful for the support of CSIRO's OCE Science Leader program and the Advanced Material transformational platform for this work. We thank Anita Hill and Marcus Zipper for their support.

The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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