

BALLAST STONE STUDIES FROM NORTH CAROLINA SHIPWRECK 003BUI, THE QUEEN ANNE'S REVENGE: MÖSSBAUER SPECTROSCOPY

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ABSTRACT

Mössbauer spectroscopy is being used to distinguish ballast stones of various rock types found in the reputed wreck of the Queen Anne's Revenge (QAR). The ultimate aim is to develop unique signatures of the stones to match with bedrocks of origin.

The most abundant stones are tholeiitic micro-porphyrific basalt, porphyritic felsic-intermediate volcanic rocks, volcanoclastic rocks, and hornblende gabbros. Initial Mössbauer studies have concentrated on the most intense spectral line each for basalts, hornblende gabbros, and porphyritic felsic-intermediate volcanic rocks. Based on quadrupole splitting (Δ) and isomer shift (δ) of samples analyzed, sixteen basalts consistently fell into one group, four hornblende gabbros into two groups, and four porphyritic felsic-intermediate volcanics into two groups. The ranges of the groups fell into two realms. Realm 1, $\Delta = 2.0$ - 2.4 mm/s and $\delta = 1.0$ to 1.3 mm/s, included all basalts, three porphyritic felsic-intermediate volcanics, two altered hornblende gabbros, plus one quartz

diorite. Realm 2, $\Delta = 2.7$ - 2.8 mm/s and $\delta = 1.1$ - 1.2 mm/s, included two unaltered hornblende gabbros plus two granites. One volcanoclastic rock was analyzed and was found to be distinctly different with $\Delta = 1.2$ mm/s and $\delta = 0.4$ mm/s.

Although individual differences can be seen among lithologic groups, it is not yet clear whether Mössbauer spectroscopy can be an effective fingerprinting technique for the identification of bedrock sources.

INTRODUCTION

Ballast stones from the reputed wreck of the Queen Anne's Revenge (QAR) are being characterized with the aim of determining their provenance. A match of the ballast with bedrocks along known routes of Edward Thatch's ("Blackbeard") travels would support other evidence that the wreck in Beaufort Inlet is indeed the Queen Anne's Revenge. Ballast stones are being characterized by rock types, whole rock major and minor element compositions, petrographic textures, age dates, and Mössbauer spectroscopy. This paper focuses on the efficacy

of Mössbauer signatures as an identifying technique for the ballast stones.

The total amount of ballast stones at the wreck site is estimated at 40 (metric) tons, based on the size of the ship. Of these, 131 stones of a total 348 kg were recovered from three separate dives on the wreck. Approximately 15,000 stones remain, if the size distribution mimics those already recovered. Although less than one percent of the ballast stones have been studied, they were recovered randomly and are considered to be somewhat representative of the ballast pile.

Mössbauer spectroscopy is a nuclear gamma ray resonance emission and absorption technique that allows characterization of materials by measuring changes in the nuclear energy levels of an atom caused by changes in its chemical environment (Dickson and others, 1986; Cranshaw and others, 1985). Mössbauer spectroscopy must be performed with a particular isotope; for these studies ^{57}Fe was the isotope of interest. In Mössbauer spectroscopy a radioactive source (in this case ^{57}Co) that decays to the isotope of interest is used to send gamma rays through a sample and into a detector. The source is set into motion to Doppler-shift the narrow-energy-width gamma ray to a range of energies. When the energy of the gamma ray matches a transition energy in the sample, the gamma ray is absorbed and then reemitted isotropically. The detector measures reductions in the intensity of radiation coming from the source (absorption peaks). It is possible to obtain multiple absorption peaks from the same sample depending on the chemical environment (crystal structure, lattice and bonding characteristics) of the sample.

The three main parameters obtainable from a Mössbauer spectrum that yield information about the structure of a material are 1) isomer shift (δ), 2) quadrupole splitting (Δ), and 3) magnetic field strength at the nucleus. The isomer shift is a measure of the s-electron density inside the nucleus and is seen in the spectrum as the shift of the centroid of an absorption peak (or group of peaks) away from the energy of the standard transition. Quadrupole splitting is a measure of the interaction between the quadru-

pole moment of the nucleus and the electric field gradient produced by the orbital electrons and the crystal lattice. This interaction causes a single peak to be split into two peaks of (usually) equal intensity. The size of the splitting is reflected in the distance between the two absorption peaks in the spectrum. The magnetic hyperfine interaction allows measurement of the internal magnetic field strength at the nucleus. In iron, this interaction causes a single peak in the spectrum to split into a group of six peaks whose intensities have a known proportionality relationship to each other. In addition to these three main parameters, the intensity and width of the absorption peaks yield information about the amount of iron at a particular site or in a particular oxidation state. Mössbauer spectroscopy has many uses in the analysis of material and minerals (Stevens and others, 1998a, b). The method has been used successfully in the determination of original firing temperature and provenance in studies of pottery sherds (Cranshaw and others, 1985; Leute, 1987; Whatley and McKenzie, 1994). The authors' experience with Mössbauer studies of clays and provenance led to the current effort using Mössbauer spectroscopy to determine the provenance of rocks in ballast stones from the wreck of the *QAR*.

BASIC ROCK TYPES

The dominant rock types of the stones recovered thus far are microporphyritic basalts, porphyritic felsic-intermediate volcanics, volcanoclastic rocks (mostly plagioclase), and hornblende gabbros. Lesser amounts of stones included altered and sheared hornblende gabbros, granites, limestones, amphibolites, and traces of a few others. So far, our Mössbauer study has concentrated on the basalts and unaltered hornblende gabbros because they are among the most abundant ballast stones and will have consistently strong Mössbauer signatures. The major rock types and their corresponding minerals with significant iron are listed in Table 1.

MÖSSBAUER SPECTROSCOPY OF QAR BALLAST STONES

Table 1. Minerals in major rock types for QAR ballast stones.

basalt	hornblende gabbro	porphyritic felsic-intermediate volcanics	volcaniclastic rocks
Ca-plagioclase augite (olivine) (biotite) (epidote) magnetite	Ca-plagioclase (clinopyroxene ¹) clinoamphibole ² (epidote) (magnetite) (sulfides ³)	Na-plagioclase clinopyroxene clinoamphibole chlorite (biotite) (epidote)	quartz Na-plagioclase clinopyroxene (biotite)

1. augite or pigeonite
 2. hornblende or actinolite
 3. pyrite, marcasite, or chalcopyrite
- minerals in minor amounts (1-10 wt.%) are in parentheses

EXPERIMENTAL

Mössbauer spectra were acquired at room temperature (20° C) from 0.5 g samples of ground (-40 mesh, 0.425 mm) ballast stones using an Elscint model MDF-N-5 Mössbauer spectrometer, a Reuter-Stokes model P3-1605-261 Xe-filled proportional detector, a ⁵⁷Co/Rh source and an ORTEC/ACE board in a personal computer. Counting times ranged from one to three days, depending on the intensity of the Mössbauer signal. Spectra were fit to sums of Lorentzian peaks with MOS Mössbauer Plot and Fit Program version 960709/A by S. Nagel and A. Khasanov. A total of 30 samples were tested; two spectra (one amphibolite and one volcaniclastic rock) could not be analyzed because they contained an insufficient amount of iron. Spectra for several stones were measured multiple times and fit independently to ensure consistency in the fitting results. All isomer shift data is reported relative to metallic (alpha) iron.

MÖSSBAUER SPECTROSCOPIC SIGNATURES

⁵⁷Fe Mössbauer spectroscopy was used for this study because of the abundance of iron in the dominant rock types. On the basis of iron

content alone, it may be difficult to distinguish between porphyritic volcanic rocks and hornblende gabbros but simple to distinguish between basalts and volcaniclastic rocks (Table 2). However, each mineral phase will have a unique Mössbauer signature, depending on the location and bonding characteristics of the iron in the crystal structure.

Table 2. Total iron content of QAR ballast stones*

	ave. wt.%	std. dev.
basalt (11)	6.6	0.5
gabbro (7)	4.4	1.3
porph. felsic-intermed. volc. (8)	4.5	1.2
volcaniclastic rocks (3)	2.0	0.3

Number of rocks analyzed in parentheses.

Sixteen of the samples studied were basalts; all were classified as microporphyritic basalts. Spectra for these samples were complex. Each spectrum was fit with three distinct quadrupole splittings and two magnetic sextets (Figure 1). A plot of the quadrupole splitting versus isomer shift for the most intense quadrupole doublet shows the consistency of the data from the microporphyritic basalts (Figure 2a). This doublet is produced by Fe²⁺ of M1 and M2 sites in the augite, and corresponds almost exactly with basaltic rocks from other regions (Table 3).

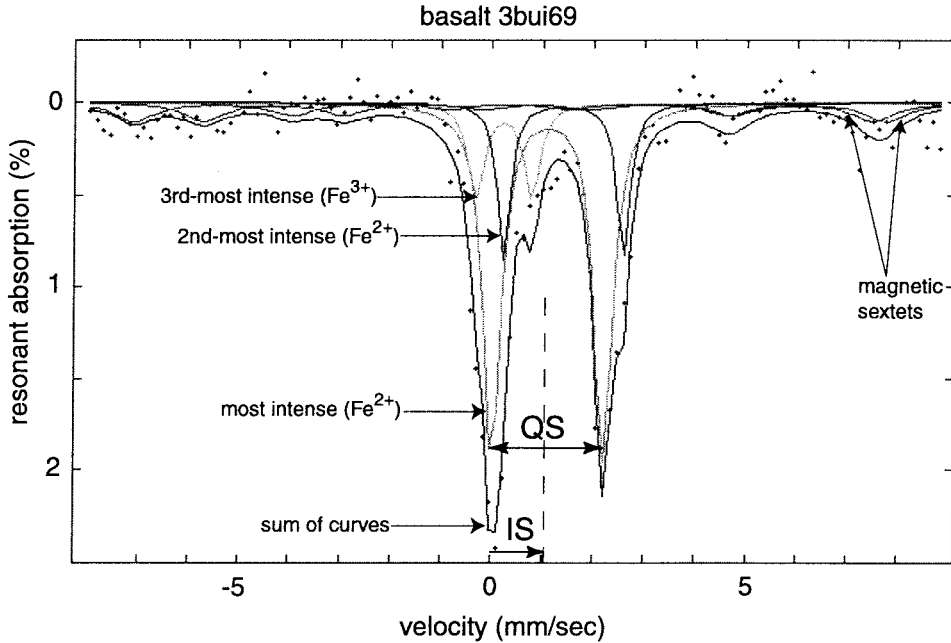


Figure 1. Mössbauer spectrum for sample 3BUI-69, a microporphyritic basalt with isomer shift (IS) = 1.403 mm/s and quadrupole splitting (QS) = 2.352 mm/s.

Four hornblende gabbro samples were analyzed. Two of the samples came from one ballast stone (3BUI-84) of unaltered hornblende gabbro, and two from a second stone (ASU 4-22-44) of altered hornblende gabbro. All samples were fit with three distinct quadrupole splittings. The most intense quadrupole splitting was found to be characteristic of hornblende (Stevens and others, 1998a, p. 308-313). Magnetic subspectra were present in the samples from ASU 4-22-44 but not in 3BUI-84. The presence of the magnetic subspectra in one stone but not the other may indicate that stones of different origin may be distinguished on the basis of the presence or absence of magnetic component, such as magnetite. A plot of the

quadrupole splitting versus isomer shift for the most intense quadrupole doublet also allows discrimination of the two gabbro forms (Figure 2b).

Four porphyritic felsic-intermediate volcanic samples were studied. Three were fit with three distinct quadrupole splittings and two magnetic sextets; the fourth was fit with two quadrupole splittings and two magnetic sextets. A plot of the quadrupole splitting versus isomer shift for the most intense quadrupole doublet distinguishes the three samples fit with three splittings and the fourth sample fit with only two (Figure 2c).

The remaining four samples were found to be quartz diorite (one sample), granite (two sam-

Table 3. Comparison of Mössbauer parameters* with other basaltic rocks

Locality	rock type	δ	Δ	reference
Karak, Jordan	basalt	1.13	2.20	(Mahmood and others, 1992)
QAR (ave.)	basalt	1.10	2.20	(this study)
Hawaii	palagonite	1.08	2.04	(Golden and others, 1993)
Bohemo-Silesian volcanic arc (ave.)	melabasanite	1.07	2.15	(Szumanska-Pajchel, 1978)
Mariana Deep	basalt	1.04	2.25	(Minai and others, 1978)
Lower Silesia	basalt	1.04	2.08	(Bakun-Czubarow and others, 1993)

*doublet from clinopyroxene Fe²⁺ M1/M2 site

MÖSSBAUER SPECTROSCOPY OF QAR BALLAST STONES

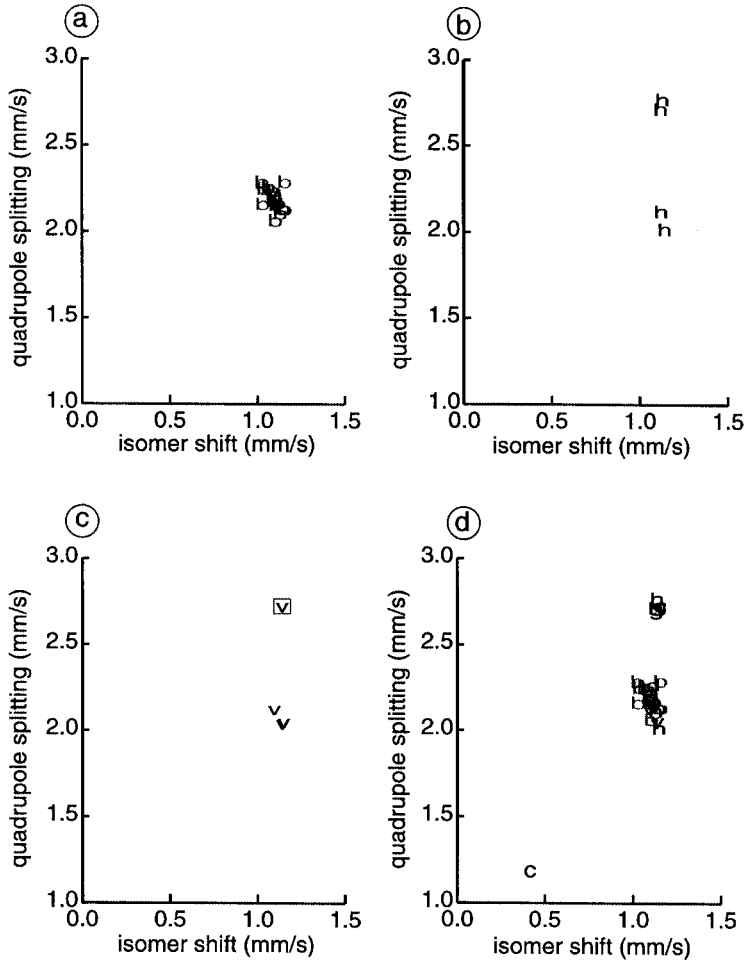


Figure 2. Quadrupole splitting (Δ) versus isomer shift (δ) for the most intense quadrupole doublet for all samples. 2a: 16 microporphyritic basalt samples. 2b: Δ of 2.5-3.0 mm/s were from altered hornblende gabbro 3BUI-84, and Δ of 2.1-2.2 mm/s were from unaltered hornblende gabbro sample ASU 4-22-44. 2c: porphyritic felsic-intermediate volcanics fit with a three quadrupole doublets each; sample with symbol enclosed in a square was fit with only two quadrupole doublets. 2d: all samples studied. Symbols are b=microporphyritic basalt, h=hornblende gabbro, v=porphyritic felsic intermediate volcanics, c=volcaniclastic, d=quartz diorite (one sample near top of basalt cluster), and g=granites (two in cluster of points at $\sim\Delta_1=2.7$ mm/s).

ples) and a volcaniclastic (one sample). The quartz and granite Mössbauer data are similar to that measured for basalts. One volcaniclastic rock was analyzed and was found to be distinctly different from the others. Figure 2d shows the quadrupole splitting versus isomer shift for the most intense quadrupole doublet for all samples studied; the volcaniclastic sample data is easily distinguishable.

The Mössbauer spectra for samples of the

same rock type were consistent. However, this study was undertaken in part to determine if samples of the same rock type taken from different locations could be distinguished. The strongest spectrum line for the basalts was nearly identical to those of basalts from other localities (Table 3), but provenance studies on rocks will rely on the presence or absence of (probably) small amounts of impurities. The Mössbauer spectra studied are already complex; it

may not be possible to distinguish the Mössbauer signatures of impurities consistently.

CONCLUSIONS

Clearly, Mössbauer data can assist in the precise characterization of rock samples. More data is needed, but this preliminary study indicates that rock types from the *QAR* wreck site considered thus far are discernable with Mössbauer spectroscopy. The combination of conventional geoscience methods and Mössbauer spectroscopy should allow the clear distinction between rock types.

It is unclear whether provenance of the rock samples will be identified by Mössbauer spectroscopy alone due to the complexity of the spectra, similarity of *QAR* basalts with others from different localities, and the probable weak intensity of impurity peaks in the data. Additional studies will be necessary before the utility of Mössbauer signatures in provenance studies becomes apparent.

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REFERENCES

- Bakun-Czubarow, N., Galazka-Friedman, J., Suwalski, J., and Szpila, K., 1993, Weathering of the lower Silesian basaltoids studied by Mössbauer spectroscopy: *Archivum Mineralogiczne*, v. 49, p. 3-21.
- Cranshaw, T.E., Dale, B.W., Longworth, G.O., Johnson, C.E., 1985, *Mössbauer Spectroscopy and Its Applications*: Cambridge University Press, Cambridge, 119 p.
- Dickson, D.P.E. and Berry, F. J. (eds.), 1986, *Mössbauer Spectroscopy*: Cambridge University Press, Cambridge, 274 p.
- Golden, D.C., Morris, R.V., Ming, D.W., Lauer, Jr., H.V., and Yang, S.R., 1993 *Mineralogy of three slightly palagonitized basaltic tephra samples from the summit*

- of Mauna Kea, Hawaii: *Journal of Geophysical Research [Solid Earth]*, v. 98, p. 3401-3411.
- Leute, U., 1987, *Archaeometry: An Introduction to Physical Methods in Archaeology and the History of Art*, VCH Publishers, New York, 176 p.
- Mahmood, S.H., Abu-Aljarayesh, I., Kofahi, M., Nasir, S., Popplewell, J., and Landyat, C., 1992, Characterization of Karak basalts using petrological, magnetic and Mössbauer studies: *Dirasat – Univ. of Jordan Serial 19B*, p. 19-33.
- Minai, Y., Takeda, M., Wakita, H., and Tominaga, T., 1978, A Mössbauer study on alteration of a deep sea basalt: *Radiochemical and Radioanalytical Letters*, v. 36, p. 199-206.
- Stevens, J.G., Khasanov, A.M., Miller, J.W., Pollak, H., and Li, Z. (eds.), 1998a, *Mössbauer Mineral Handbook: Mössbauer Effect Data Center*, Asheville, NC, 527 p.
- Stevens, J.G., Khasanov, A., Miller, J.W., Pollak, H., and Li, Z., 1998b, Documentation and evaluation of Mössbauer data for minerals: *Hyperfine Interactions*, v. 117, p. 71-81.
- Szumanska-Pajchel, B., 1978, The Mössbauer spectroscopy of natural and heated basaltic rocks: *Acta Geophysica Polonica*, v. 26, p. 327-337.
- Whatley, K.M., and McKenzie, K.P., 1994, Mössbauer studies of prehistoric Cherokee pottery sherds, *Hyperfine Interactions*, v. 91, p. 679-683.