An Open-Water Electrical Geophysical Tool for Mapping Sub-Seafloor Heavy Placer Minerals in 3D and Migrating Hydrocarbon Plumes in 4D

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***Abstract*— A towed-streamer technology has been developed for mapping placer heavy minerals and dispersed hydrocarbon plumes in the open ocean. The approach uses induced polarization (IP), an electrical measurement that encompasses several different surface-reactive capacitive and electrochemical phenomena, and thus is ideally suited for mapping dispersed or disseminated targets. The application is operated at sea by towing active electrical geophysical streamers behind a ship; a wide area can be covered in three dimensions by folding tow-paths over each other in lawn-mower fashion. This technology has already been proven in laboratory and ocean settings to detect IP-reactive titanium- and rare-earth (REE) minerals such as ilmenite and monazite. By extension, minerals that weather and accumulate/concentrate by a similar mechanism, including gold, platinum, and diamonds, may be rapidly detected and mapped indirectly-- even when dispersed and covered with thick, inert sediment. IP is also highly reactive to metal structures such as pipelines and cables.**

Currently, the only means for mapping an oil-spill plume is to park a large ship in the ocean and drop a sampling string over the side, requiring hours of time per sampling point. The samples must then be chemically analyzed, adding additional time and expense. We believe that an extension of the marine IP technology could also apply to rapidly mapping both seafloor-blanket and disseminated hydrocarbon plumes in the open ocean, as hydrocarbon droplets in conductive seawater are topologically equivalent to a metal-plates-and-dielectric capacitor. Because the effective capacitance would be frequency-dependent on droplet size, the approach we advocate holds the potential to not only map, but also to characterize the evolution and degradation of such a plume over time. In areas where offshore oil field development has been practiced for extended periods, making IP measurements from a towed streamer may be useful for locating buried and exposed pipelines, as well as pipeline leaks. We believe this technique will be a more cost-effective method than drop-sampling to map and monitor hydrocarbon plumes in open ocean settings.

A marine induced polarization system was used successfully to map a 15 km x 45 km swath of the ocean floor off eastern South Africa with 3-meter sampling along 200-meter-separated profiles. The survey detected titanium-bearing sands up to 15 meters below the seafloor. From preliminary laboratory work it is apparent that we can extend this technology to monitor significant environmental problems including anthropogenic and industrial waste washed into sensitive estuaries and sounds during storm-water runoff episodes, and also to map and characterize dispersed oil plumes in the seawater column in three dimensions, as well as movement and dispersal of both over time.

Keywords—tracking hydrocarbon plumes; seafloor minerals; induced polarization; sub-seafloor mapping; electrical geophysical tool; heavy placer minerals; hydrocarbons in seawater

I. INTRODUCTION

Induced Polarization (IP) is a current-stimulated (induced) electrical phenomenon that has been observed in certain earth materials for nearly a century [1]. It is manifested as either a delayed voltage response (a transmit-receive phase shift usually given in milliradians) or as a frequency-dependent change in received amplitude response, the so-called Percent Frequency Effect or PFE [2], [3], [4]. Often—but not always—these two different manifestations correlate closely with each other. IP is commonly used to explore for and map large disseminated sulfide deposits using a pair of transmitter electrodes to induce current flow in the ground, while the received signal is measured at a distance with a pair of non-polarizing electrodes (e.g., Ag-AgCl). In addition to sulfide minerals, IP effects have been observed in certain clays, buried metal fragments, buried pipelines and cables, and certain other minerals, most notably ilmenite (FeTiO3) and monazite ([Th, Ce, La]PO4) [5]. It is thus potentially an important tool for mapping rare-earth elements (REEs) on continental shelves. Importantly, IP is a surface-reactive phenomenon, meaning that the finer-grained a reactive material is, the more surface is exposed to the surrounding electrolyte for the same mass, and therefore the greater would be the IP effect. The causative electro-chemical phenomena can be of several types including a Warburg double-layer impedance and the so-called membrane effect [2], but they all behave as a capacitance. The IP effect is thus particularly well-suited to, and has mainly been used for, the

search for disseminated sulfides in large porphyry intrusive systems.

The USGS has developed a means for applying IP in a marine environment. This required overcoming complex issues such as grounding, the highly conductive character of seawater, array-placement and stabilization, streaming potential, and electrical noise inherent to a metal ship traveling in the sea [6], [7]; Fig. 1. In 2007 a commercialization agreement was signed and the USGS-patented technology licensed for a large and successful sub-seafloor mineral exploration and mapping effort off South Africa. This paper presents results that show the technology can also be applied to mapping anthropogenic waste and UneXploded Ordnance (UXO) on or beneath the seafloor, and possibly dispersed hydrocarbons in seawater.

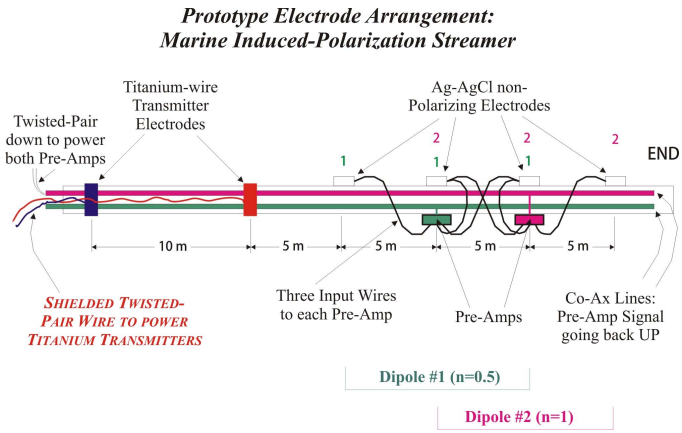

Figure 1. A towed streamer design used to make induced polarization measurements on the seafloor. On-board data-acquisition electronics, cable shielding, and floating ground not shown.

II. Mapping Ilmenite Offshore South Africa

In 2007 a six-week-long commercial marine IP survey was conducted by Williamson & Associates and Zonge International off the coast of South Africa. The objective of this large survey was to map ilmenite (FeTiO3), a highly polarizable oxide of titanium that had weathered out and migrated offshore from where on-land ilmenite mining operations are now ongoing [8], [9], [10].

Fig. 2 shows the amount of heaver placer minerals from a vibracore survey carried out during an earlier offshore survey. Note especially the feature labeled "Northern Paleochannel."

Fig. 3 shows IP chargeability for the outlined part of Fig. 2. This is a small subset of a much larger geophysical survey over the area; note the scoured paleo-channel manifesting residual ilmenite in the upper left of the figure (seen as lighter blue immersed in the darker blue "barren" shallow-water sands). Water depths in this survey area reach up to 45 meters; the paleo-channels stem from previous glacial low-water stands where these river channels extended to a coastline much farther east. The IP-reactive ilmenite originates from a weathering source on land (upper left; shown in Fig. 2) to higher density deposits on and beneath the seafloor (yellow and orange, lower right). Most of the ilmenite deposit thus appears to lie offshore (the warmer colors in the center and lower right side of the image), much of it distributed south and southeast by the long-shore Agulhas current and buried under later, inert sediments. This survey provided a vast new area to explore for titanium; by using multiple receiver dipoles, the survey array provided four depth-slices, one for each transmitter-receiver N-spacing. Modeling shows the peak-responses for the first three N-spacings were 5 meters for N = 1; 8 meters for N = 2; and 11 meters for N = 3. There was still a 20%-of-peak response at about 24 meters depth for N = 3.

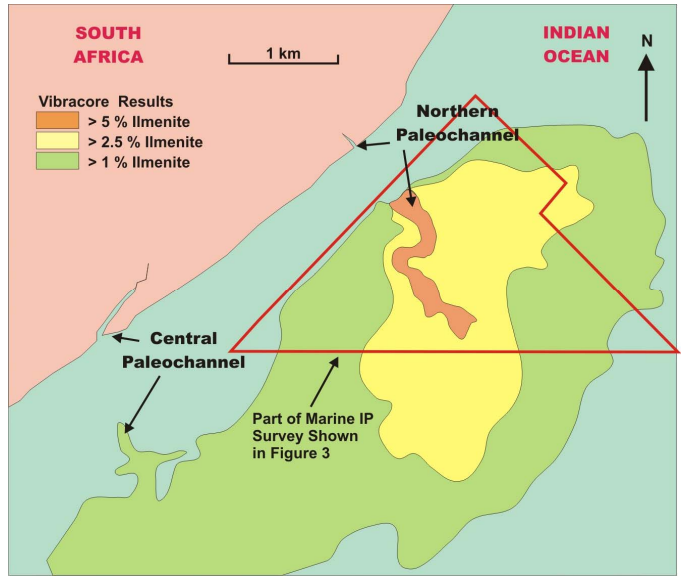

Figure 2. Economic heavy minerals mapped offshore South Africa using vibracores; compare Figure 3.

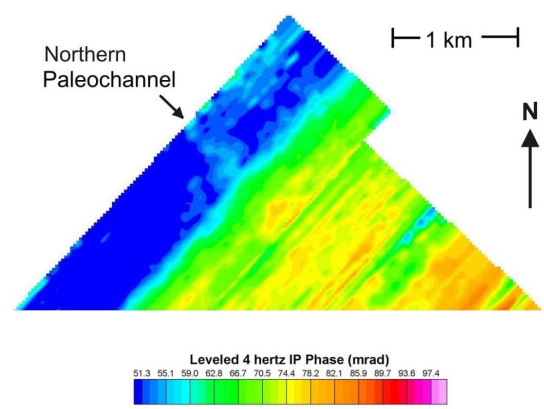

Figure 3. The IP phase-shift at 4 Hz for the N = 1 (shallowest) dipole separation for part of the area shown in Fig. 2. Note the corresponding shape of the northern paleo-channel in the lighter blue color (residual ilmenite) immersed in the dark blue low-chargeability coastal shallows. NE-SW striping is an artifact of the strong current in the area. This constrained ship-movement in those directions; additionally, a decision was made to not filter the IP data.

III. UneXploded Ordnance

Data from several sea-trials suggest it is possible to use marine IP to map offshore UXO. The example in Fig. 4 is part of a towed-streamer profile carried out on the east side of Cat Island, south of Biloxi, Mississippi. Here a coincident resistivity - IP anomaly ("Metallic Object" in Fig. 4) was observed in a small area from where a Swedish bronze cannon

had earlier been dredged, one of many such cannon apparently lost with a Spanish sloop that reportedly sank during a 17th Century hurricane 11. This figure shows one profile using a 10-meter electrode separation dipole-dipole (four-electrode in-line) array.

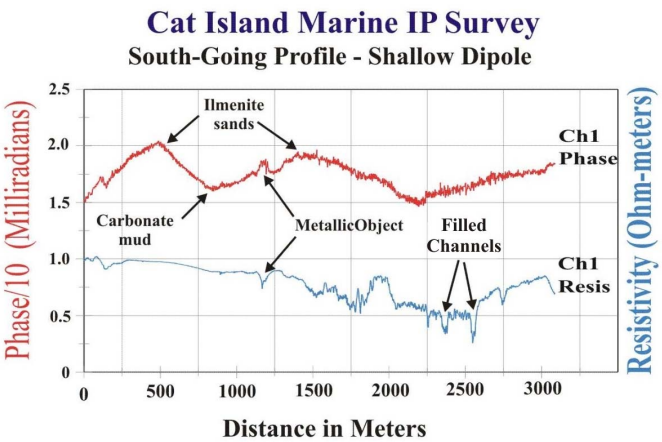

Figure 4. An IP anomaly coincident with a resistivity low identifies a buried metallic object where a bronze cannon had been dredged earlier. Filled channels, on the other hand, exhibit resistivity lows but do not exhibit an IP anomaly.

Note that the IP-reactive target (probably an additional bronze cannon) can be detected considerably more than 10 meters away from the center of the anomaly; we ascertained this by looking at deviation from zero approaching and leaving the anomalous zone, assuming that the anomaly was caused by a point-source. Note also that dredged and subsequently hurricane-refilled channels ("Filled Channels" in Fig. 4) on the same profile show similar resistivity anomalies (when scale is magnified these appear flat-bottomed), due to greater porosity from lower compaction - but there was no IP anomaly.

Another survey conducted offshore of Murrells Inlet in South Carolina (Fig. 5) shows an increasing density of short-wavelength IP anomalies as one approaches the ship-channel from each side. The geographic density and distribution of this apparent "noise" suggest it is likely due to metallic trash discarded by returning boats. The Cat Island example indicates that IP responds to bronze, and the Murrells Inlet survey shows multiple IP responses caused by what is likely metallic trash on and beneath the seafloor. A sea-trial in Puget Sound showed strong IP responses as we passed over buried cables. Together with laboratory experiments, these suggest that marine IP can be effective at locating exposed as well as buried UXO on and beneath the modern seafloor—including non-ferrous materials.

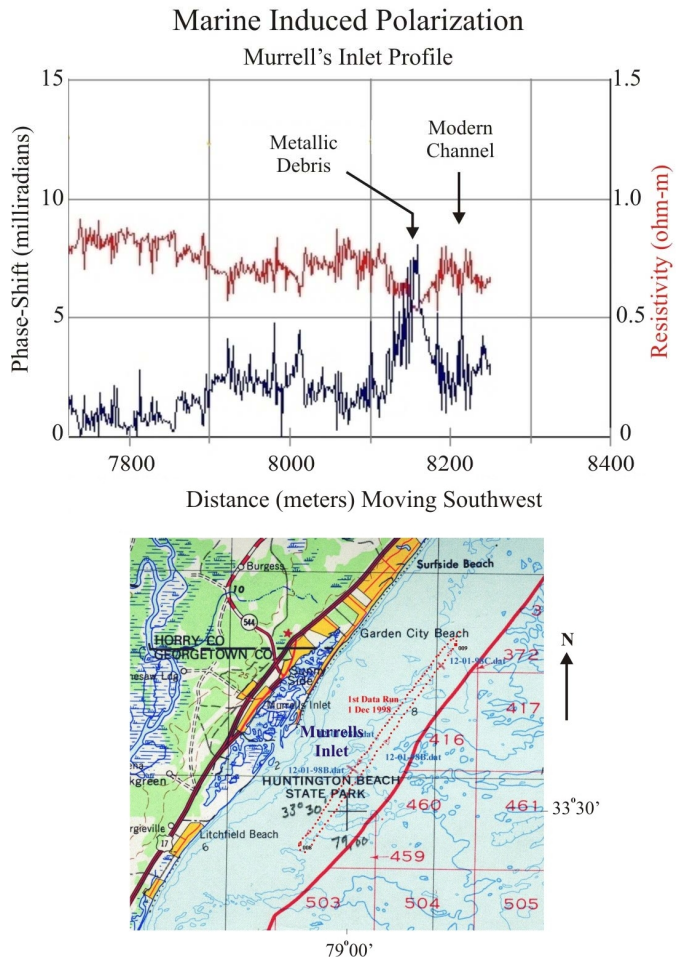

Figure 5. A marine IP profile across the entrance to Murrells Inlet, South Carolina. The ship track was from northeast to southwest, and a coincident IP high and resistivity low indicate a probable wreck (red dash below "Inlet" on dotted ship-track).

IV. Laboratory Evidence

Grab samples collected in Long Island Sound during a Woods Hole Oceanographic Institute cruise [12] were later analyzed in a USGS laboratory for their IP spectra—that is, the IP response over a wide frequency range. These samples contain anthropogenic sludge that emanated from the Connecticut River over the past several centuries. The sludge has high carbon content and is thus self-reducing, mainly due to its high biological content. The sludge also includes a small, very fine-grained metal content, along with *Clostridium perfringens* spores. Both of these are considered a threat to wildlife and humans on the north shore of Long Island [13]. The *C. perfringens* bacterium is considered particularly dangerous to humans, giving rise to symptoms ranging from food poisoning to gas gangrene. Laboratory measurements were carried out on grab-samples using an acrylic sample-holder with electrode grids placed at both ends in a modified Wenner configuration [2]. Extraordinary safety precautions were necessary for measuring these samples, including mask

and gloves. This laboratory had to be systematically decontaminated once the measurements were complete.

Fig. 6 shows a combined example of two IP spectra measured in the laboratory. The small cluster ("+") in the lower right is the calibrate IP spectra for inert, crushed optical glass, portrayed in the Cartesian complex plane. The crushed glass is placed in an acrylic container described above and measured with saltwater only; as silica is non-polarizable, grain size is irrelevant. The glass sample measurement is necessary, and serves as a calibration of the system, as induction from wires and other hardware must be removed from subsequent measurements to obtain meaningful spectra. Electrode spacing is standardized for all samples with the acrylic cell; spectral measurements have been shown to be independent of the electrodes as long as a standardized array is used.

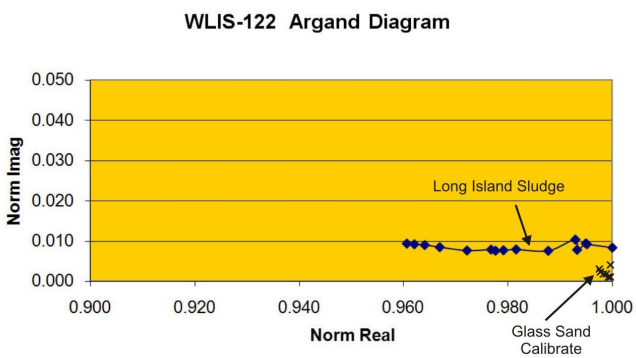

Figure 6: Argand or Cole-Cole diagrams of (+) a glass-sand calibrate sample and (♦) a sludge grab-sample from Long Island Sound. Frequencies used range from 0.125 Hz on the right side to 72 Hz on the left. The calibrate shows that the system noise is about 0.6 percent. The IP spectrum for the sludge sample shows significant amplitude variation with frequency (the Normalized Real component variation on the horizontal or X axis of 4 percent), and a distinctive, "flat" shape with little variation in the vertical (Normalized Imaginary or phase-shift component) on the vertical (Y) axis.

The calibrate spectrum was acquired and deconvolved from subsequent sample measurements [2], [8]. The "Normalized Imaginary" (Y) axis represents a time-delayed phase shift in milliradians characteristic of polarizable material (such as clays, metallic fragments, sulfide minerals, certain titanium oxides and REEs, etc.). The "Normalized Real" (X) axis shows the received amplitude as it changes with frequency (often called a "percent frequency effect"). Curves are normalized to the lowest frequency. This is often called an Argand or Cole-Cole diagram [14], and is an excellent way to visualize the spectral character of an induced polarization source. A calibration Argand or Cole-Cole diagram using crushed optical glass shows that noise in this system is less than 0.6 percent.

Fig. 6 also shows an example IP spectrum from one of the anthropogenic sludge grab samples from Long Island Sound ("♦"). Note that the Normalized Imaginary (phase shift or Y-axis) remains relatively constant over the 0.125-72 Hz frequency range, while the amplitude of the detected IP signature varies by 4.0 percent. This is a moderate IP anomaly by land-based IP standards, and the "flat" spectral signature in the Cole-Cole diagram is apparently diagnostic of this anthropogenic waste (several samples show it). Since Argand diagrams for individual mineral species tend to peak at mineral-specific frequencies ranging from 0.1 Hz to 8 Hz, it is likely that this curve represents responses from at least two, and likely three different metallic-sulfide and metal species (for instance, pyrite and pewter).

V. Mapping Hydrocarbons in the Open Sea

The Macondo Well blowout of April–July, 2010 in the Gulf of Mexico has given pause to nearly all deepwater drilling in the United States. The main issue remaining: where did 200,000,000+ gallons of released oil go? Raw hydrocarbons normally have a range of gravity and volatility. It appears that some of the Macondo Well blowout product floated to the surface, some sank, and some has been reported drifting over vast distances in the deep water column [15], [16]. The situation was further complicated by the release of huge quantities of Corexit, an oil dispersant with poorly-understood impact on aquatic and benthic life. Technology currently used to track these hydrocarbons ranges from dragging chains across the shallow seafloor to posting a $100,000/day vessel for several hours at a single location while a sampling line is lowered and retrieved. Sample bottles collected must then be analyzed, and the results provide only a single data point on a target that is both moving and evolving with time. This is remarkably inefficient [17].

A consideration of the topological equivalence of a metal-plate capacitor with an oil-based dielectric, and a dispersed oil plume in highly-conductive seawater (Fig. 7), suggests that it is possible to use a modified IP system to map seawater capacitance and thereby track the plume. Basic physics would suggest that the peak frequency response of the dispersed hydrocarbons would correlate with droplet size. Experiments in sea-trials [10] indicate that a towed array such as shown in Fig. 8 should be able to sample a vertical 2-D slice of the seawater column at about 3–4 knots, at a resolution controlled by the transmit square-wave frequency. If the tow-path is folded over itself in lawn-mower fashion, it should be possible to rapidly map a drifting hydrocarbon plume in near real-time—in other words, in four dimensions. In shallow water, temperatures should allow bacterial action on the hydrocarbons, but this is less likely in deep, cold waters. In shallow water, there would likely be degradation of the dispersed hydrocarbons with time for at least some of the plume. As the dispersed elements of the plume evolve and possibly degrade this way with time, droplet-size characterization could be measured via the peak frequency response and its breadth. This means that this marine capacitive system should be able to both rapidly map a drifting, dispersing hydrocarbon presence, as well as characterize how it evolves over time. Laboratory experiments are currently underway, and point-sampling would still be necessary to verify results from a towed-streamer array.

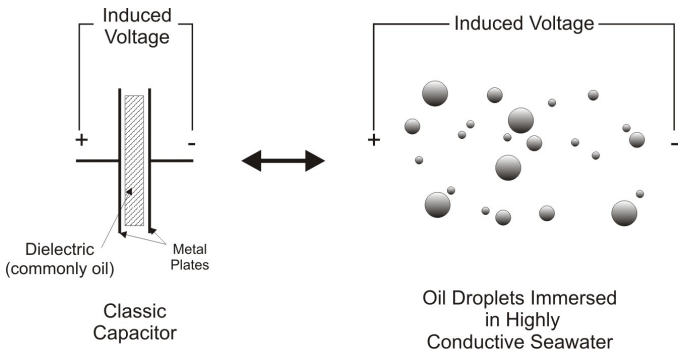

Figure 7. Topological equivalence of a classic capacitor vs. dispersed oil immersed in conductive seawater.

VI. Conclusions

The induced polarization effect is a surface-reactive physical property; there are several different physical phenomena giving rise to it, including Warburg impedance, electrode effects, and the so-called membrane or clay effect. Because IP is surface-sensitive, disseminated metals and metallic-luster minerals like sulfides, ilmenite, and monazite will provide a much stronger reactive response than an equivalent volume of the same mineral in the form of a solid block. This means that the IP effect can be used to identify and characterize (using IP spectral signatures) sediments with relatively small percentages of these reactive materials; on land this can be as little as 0.1 percent by volume for ilmenite.

IP measurements have been shown over the past several decades to directly detect ilmenite, monazite, metal in most forms, and sulfides on and beneath the seafloor. IP can also serve as a proxy for mapping self-reducing anthropogenic sediments on or beneath the seafloor through the entrained, extremely fine-grained sulfides and metallic content always found in sewage (Wynn and Grosz, 2000; Wynn and Roberts, 2009).

Laboratory and limited sea-trial data support several conclusions about the use of marine induced polarization:

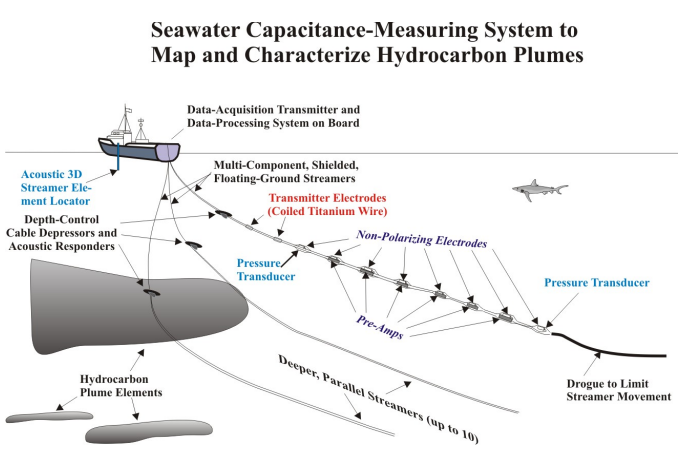

Figure 8. One of several possible configurations for mapping and characterizing a dispersed hydrocarbon plume, accomplished by measuring seawater capacitance (DOI patent pending).

1) Ocean-floor sulfide minerals—especially the known widely dispersed and disseminated sulfide halos undetectable using EM and resistivity methods—can readily be mapped using this approach. Observations of IP phase shifts at considerable distances from massive sulfides in the Bismarck Sea suggest that marine IP can be a cost-effective tool for locating these sulfide deposits even if the detection system is a kilometer or more away.

2) Ocean-floor titanium-sand and heavy placer resources can be mapped to depths of at least 15 and up to 24 meters beneath the seafloor in three dimensions using a staggered-electrode dipole-dipole array (Figure 1). Depth-slices of IP chargeability were thus obtained from a large area off the coast of South Africa, showing a vast new titanium resource there in three dimensions.

3) While evidence is sparse (fragments of buried wrecks and buried cables detected thus far during sea-trials), basic physics also suggest that marine IP should be an excellent tool for mapping UXO on and beneath the ocean floor. Current methods for searching for underwater ordnance are almost exclusively magnetic; any non-ferrous target is largely invisible to this approach. EM or resistivity techniques are generally not applicable, as the potential target would be a conductive metal anomaly buried in a sea of highly-conductive (0.25-ohm-meter) saltwater.

4) Cables and pipelines trenched into the ocean floor in pre-GPS time can be accurately mapped using marine IP.

5) Platinum is found in intimate association with ilmenite in anastomosing streams in Union Bay off of Freetown, Sierra Leone; gold is also found with ilmenite at the bottom of panned sediments from rivers in Venezuela and in southern Alaska. These together suggest that marine IP is a potential fast proxy exploration tool in the search for precious metals and diamonds in the near-offshore sub-seafloor.

6) Physical principles suggest that a specially-configured, towed-IP array should be able to map and characterize a dispersing hydrocarbon plume in the open ocean, and track it over time to see if it degrades by measuring the frequency-dependence of the seawater capacitance; a US patent has been applied for.

References

[1] Schlumberger, C., 1920, Ētude sur la prospection électrique du sous-sol: Gauthier-Villars, Paris.

[2] Sumner, J.S., 1976, Principles of induced polarization for geophysical exploration: Elsevier, New York.

[3] Kearey, Philip, and Michael Brooks (1991). An Introduction to Geophysical Exploration, 2nd edition, Blackwell Science, New York.

[4] Zonge, K.L., Wynn, J.C., and Urquhart, S.A., 2005, Resistivity, induced polarization, and complex resistivity: chapter 9 in the Society of Exploration Geophysicists Special Volume on Near Surface Geophysics, p. 265 - 300.
[5] Wynn, J.C., 1988, Titanium geophysics-- a marine application of induced polarization: Geophysics, v. 53, p. 386 - 401.
[6] Wynn, J.C., 1998a, Induced Polarization technology in the marine environment. U.S. Patent 6,236,211 B1 (May 2001).
[7] Wynn, J.C., 1998b, Induced polarization detection system for identifying metals and minerals on the ocean floor. U.S. Patent 6,236,212 B1 (May 2001).
[8] Wynn, J.C., Grosz, A.E., and Foscz, V.M., 1990, Induced polarization and magnetic response of titanium-bearing placer deposits in the southeastern United States: in: Society of Exploration Geophysicists Special Volume on Induced Polarization, p. 280 - 303.
[9] Wynn, J.C., and Grosz, A.E., 2000, Induced polarization - a tool for mapping titanium-bearing placers, hidden metallic objects, and urban waste on and beneath the seafloor: Journal of Environmental and Engineering Geophysics, v. 5, p. 27 - 35.
[10] Wynn, J.C., and Roberts, Will, 2009, The Application of Induced Polarization Techniques to Detect Metal-Bearing Offshore Anthropogenic Waste and Unexploded Ordnance: Proceedings of the Symposium for the Application of Geophysics to Environmental & Engineering Problems, Ft. Worth, TX, 29 March-2 April 2009, p. 1104 - 1113.
[11] John Woolsey, Mississippi Mineral Resources Institute, Oxford, MI, oral communication, 1998.
[12] ten Brink, Marilyn, and Johan Varekamp, 1999, USGS CMG 99056 Metadata: United States Geological Survey, Woods Hole, Massachusetts. Data (navigation) of field activity 99056 (C-56-99-LI) http://walrus.wr.usgs.gov/infobank/c/c5699li/html/ c-56-99-li.meta.html
[13] Mecrey, E. in Long Island Sound from 11/08/1999 to 11/11/1999 L., and Bucholtz- ten Brink, M.R., 2000, Contaminant distribution and accumulation in the surface sediments of Long Island Sound: Journal of Coastal Research 16, p. 575 - 590.
[14] Cole, K.S., and R.H. Cole, 1941, Dispersion and absorption in dielectrics. Journal of Chemical Physics, v. 9, p. 341 - 351.
[15] Schrope, Mark, 2010, Upbeat oil report questioned: Nature 466, (12 August 2010), p. 802.
[16] Dybas, C., Kenney, J.; and Murphy, S., 2010, Scientists map origin of large underwater hydrocarbon plume in Gulf: National Science Foundation News, Press Release 10-148, 9/15/2010, 5 p.
[17] Wynn, J.C., 2011, Measuring Seawater Capacitance In Three Dimensions As Well As Time: US Patent Applied for (provisional number 13/091,314): 21 April 2011, 26 pages, 4 figs.