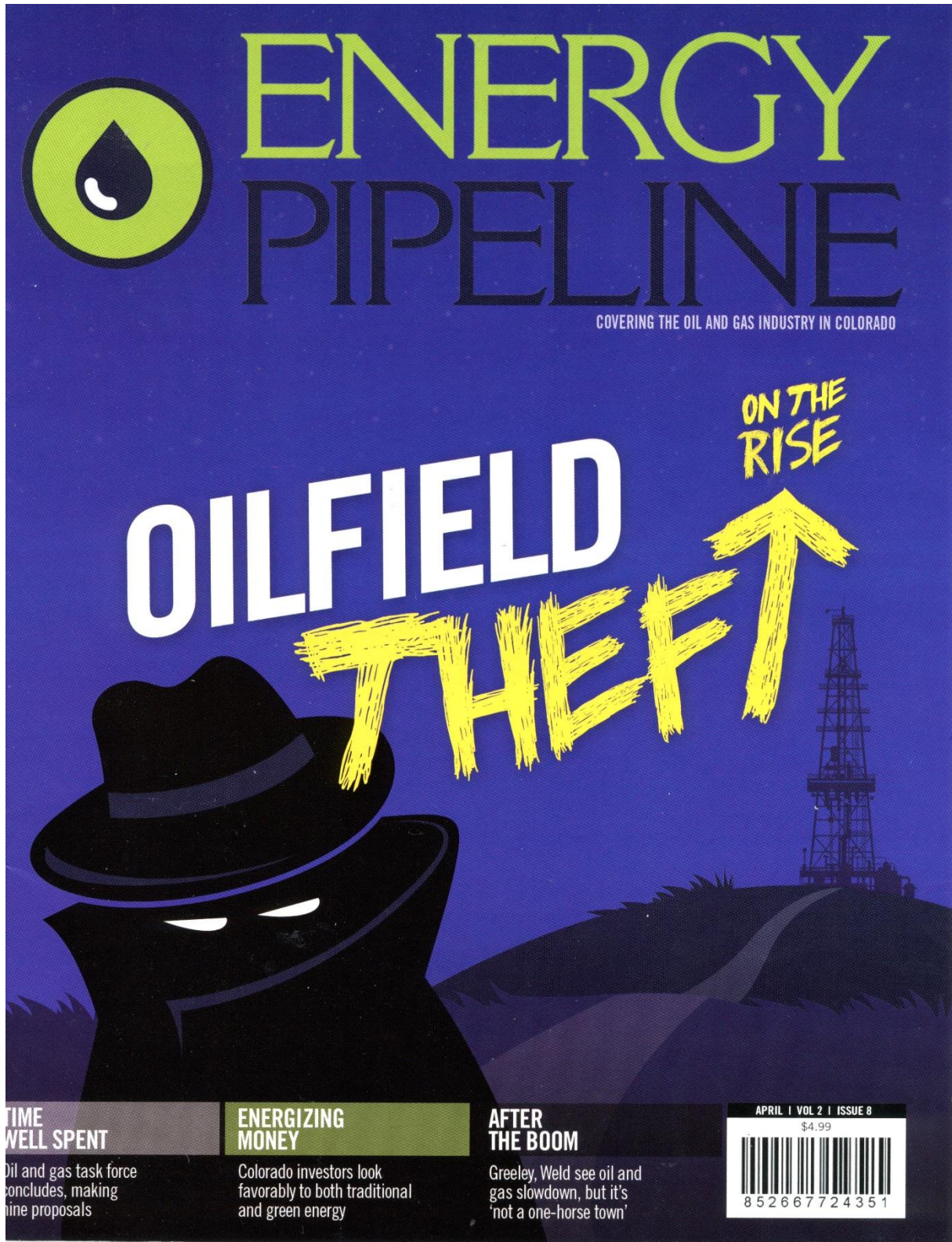




ENERGY PIPELINE

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TECH TALK

UNLOCKING CHEMICAL ANCESTRY THROUGH STABLE ISOTOPES

BY GARY BEERS • FOR ENERGY PIPELINE

WHILE A DNA TEST can unlock a biological history to provide unique identities and to display ancestral connections, a parallel more powerful and comprehensive test is experiencing breakout use in many activities to unlock the chemical history of living and nonliving materials. Stable isotope analysis is experiencing increasing widespread application in many activities.

In 1977, the first article was published on the use of stable isotopes analysis (SIA) to answer archaeological questions. Since then, especially after the turn of the century, uses of SIA have exploded in number and infused into many areas of investigations, especially as a new powerful tool in the red-hot field of forensic science.

Let's look at a few of the interesting uses that impact everyday life.

FOODS

- Can the "organic" status of vegetables be assured?

Instead of relying on the claim that the vegetables are grown under organic farming practices (i.e., no synthetic fertilizers, no applications of pesticides), agricultural experts in New Zealand have used SIA to answer this question. Using measurements of nitrogen and carbon isotopes, there is a clear distinction between organic and conventionally raised vegetables. However, this approach does not work for leguminous vegetables (i.e., peas) that fix their own nitrogen from the atmosphere.

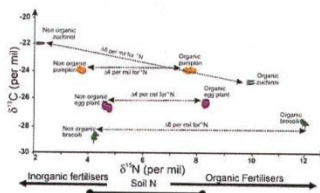
Is your food adulterated or the source mislabeled?

Did you buy synthetic vanilla flavoring sold as the natural extract, real maple syrup cut with molasses, expensive wine that has been diluted with a cheaper wine?

Did you buy expensive wild salmon that was farmed or illegally poached, valuable olive oil that did not come from Italy, or cheap single-malt whiskey intentionally mislabeled as an upscale brand?

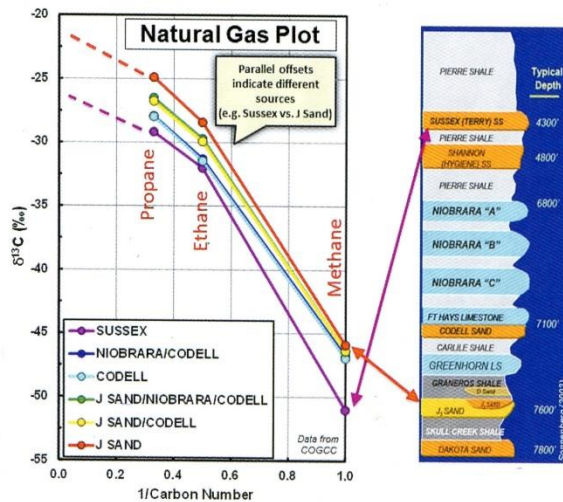
Chemists can now use SIA to answer questions about the composition and origin of food, even though the most sophisticated chemical analyses cannot provide these identities.

- Analyses of narcotics (i.e., heroin, cocaine, cannabis, steroids) and other drugs can be submitted for SIA analyses to determine origin and/or manufacturing source. For example, a man was initially arrested on the street for possessing five tablets of ecstasy. Suspicious, the police obtained a search warrant and found a hidden bag containing thousands of ecstasy tablets. Since the man claimed the bag was not his and belonged to a friend, the police needed more information for a conviction. SIA was performed on both sets of tablets and the isotopic profiles were identical.
- Natural variation in explosive materials often hampers clear conclusions. SIA of explosives, including burnt match sticks from an arsonist's fire, can provide valuable information on the composition and origin of these materials.



For over 50 years, **GARY BEERS**, has worked in numerous fields of environmental science as a consultant, regulator and educator. This career included senior management position with major consulting, nonprofit and public organizations. He has founded several successful firms to capture emerging resource management markets. One of his latest ventures, EnviroScienceINFO, provides content for public media.

TECH TALK



- A substantial amount of precise information on the origin of the cotton fiber in the paper and ink used to produce counterfeit paper money can be obtained from SIA.
- The origin of jewels can be revealed with SIA. For example, researchers have a difficult time pinning down the source turquoise using trace element analyses, since these components vary too much within mines to allow precise source identification. In 2008, a breakthrough occurred when a researcher used SIA to confirm the origin of a piece of turquoise.

The longest history, over 30 years, for the use of SIA exists in the fields of archaeology and anthropology, especially the identification of the origin of the heritage materials.

HUMAN

We are what and where we eat and drink.

The immense analytical power of SIA is best seen in uses to identify the dietary habits and where one has lived and traveled during their lifetime. Every molecule in our bodies is made up of not just different elements, but of different ratios of stable isotopes of these elements.

As we age, certain tissues only form during a

specific time and others are continually renewed and are built of what is being presently consumed. Thus, as shown in Graphic 2, teeth and bone tissue contain permanent information on what we ate and where we were during specific time periods of our life - and hair and fingernail tissues provide a moving, recent snapshot of these properties.

A fascinating article was published in 2014 ("Multi-isotope analysis demonstrates significant lifestyle changes in King Richard III", *Journal of Archaeological Science* 50:559-563). He lived from 1452 to 1485 and his remains were excavated in August 2012 - some 527 years after his burial. Based on an SIA of his remains, a description pieced together his diet, geographical movements, and periods of residence. Interesting results are from the 26-month period when he became King of England and his life changed. This research using SIA provided a rare opportunity to cross-reference science-based archaeology with history.

While full of technical jargon, this paper is worth a read.

CRIMINAL INVESTIGATIONS

The use of SIA is emerging and rapidly expanding in law enforcement, including finding who is the unidentified body.

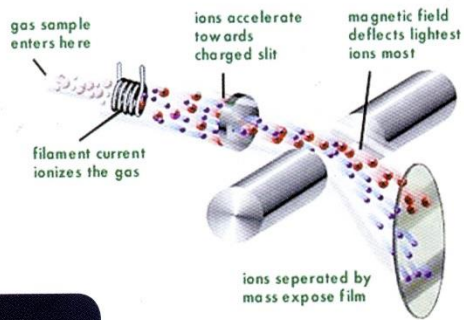
FACTS
STABLE
ISOTOPE

ISOTOPE

Forms of same element that have the same chemical properties and only differ in relative atomic mass (i.e., each as different numbers of neutrons). All isotopes behave the same way in chemical reactions.

STABLE
ISOTOPE

An element that does not change over time (i.e., does not decay).



ABOUT BLE OPES

ISOTOPE MEASUREMENT

Isotopes are measured using the differences in mass and can not be measured using chemical analysis for the element. An instrument called a mass spectrometer. For example, a sample of carbon is analyzed and the relative percentages of each stable isotope (i.e., carbon-12 and carbon-13) are determined.

One outcome is the improved evaluation of physical evidence. As an example, white paint chips were found at a crime scene and were chemically matched to white paint on the walls of the suspect's home. However, SIA testing revealed that the two samples of paint were made in different factories. Thus, an innocent individual was cleared of the crime.

Another outcome is expressed by one of the world leaders in this field (Dr. Wolfram Meier-Augenstein, James Hutton Institute, Scotland) who recommends viewing each stable isotope as a filter to aid focusing other forensic tools:

"In our globalized world, a John Doe could have come from anywhere. Investigators start looking for clues close to where the victim was found, but if nothing turns up, they could end up combing through every missing persons list in the world. Stable isotopes narrow that search. Deuterium and oxygen-18 from a victim's hair or fingernails can exclude 80 percent or 90 percent of the world. A nitrogen-15 analysis of the victim's muscle tissue could reveal that he was a vegetarian, another useful clue. And heavier isotopes such as strontium leach from rocks and make their way into our bones and teeth.

Together, all these clues narrow the field of potential matches, greatly simplifying things for detectives. We don't find a needle in a haystack. What we do is, in an ideal circumstance is reduce the haystack to a manageable size."

SIA of hair is proving to be an emerging powerful forensic tool. Isotopes from current diet and environmental location are locked into the base of a hair strand as it grows. The analysis of how the isotopes change along a hair strand can reveal a person's recent food habits and extent of travel.

ECOLOGY

One of the prime uses of SIA in ecology is to construct a timeline of how and when populations of herbivores migrated and reacted to changes in the types and abundance of different types of vegetation.

EARTH SCIENCES

Stable isotopes are indispensable for nearly every earth science discipline. For example, they are useful in tracing the water cycle, and used to help understand geological processes at low and high (deep subsurface) temperatures. Probably most notable are the uses of stable isotopes of oxygen, carbon and sulfur for understanding the past climate on earth on variable time scales (historic, prehistoric, quaternary and deep time). More specifically, oxygen isotopes of biologically precipitated calcites (foraminifera, corals, mollusks) and occasionally inorganically precipitated ones (limestone cave formations, speleothems) can be used to interpret the temperature during precipitation. In environments where temperatures vary very little (the deep sea), oxygen isotopes of carbonates can be used to infer the presence or absence of ice cover at the Earth's poles. Carbon isotopes of these carbonates track large perturbations in the carbon cycle.

WIDESPREAD USE IN OIL AND GAS EXPLORATION

SIA when applied to natural gases from different formations in a basin can identify whether the origin of the gas is biogenic (i.e., low value gas at shallow depths generated by bacterial metabolism and unrelated to processes that form oil) or is thermogenic (i.e., high value gas at deeper depths generated by thermal breakdown of organic matter). Thermogenic gas is a strong indicator of a petroleum pay zone in a formation.

The results from SIA of natural gases from several formations in the Wattenberg Field are graphed in graphic 3. These are thermogenic gases and those from the deeper formations exhibit the presence of a higher quality of petroleum. If biogenic gas was present, the plotted values would be lower than minus 60.

Besides their value to exploration, the SIA can identify the petroleum sources contributing to spills and/or placed in disposal areas. A forensic investigation of accidental discharge of oil-based drill cuttings onto the seabed of Norwegian North Sea, after eight years of exposure to biodegradation and weathering was able to identify several sources from drilling operations. (Reference: Source identification of oil-based drill, cuttings on the seabed based on stable carbon isotopes. Environmental Chemistry Letters, B. Skaare, M. Schaanning, and P.T. Morkved, 2008). ♦