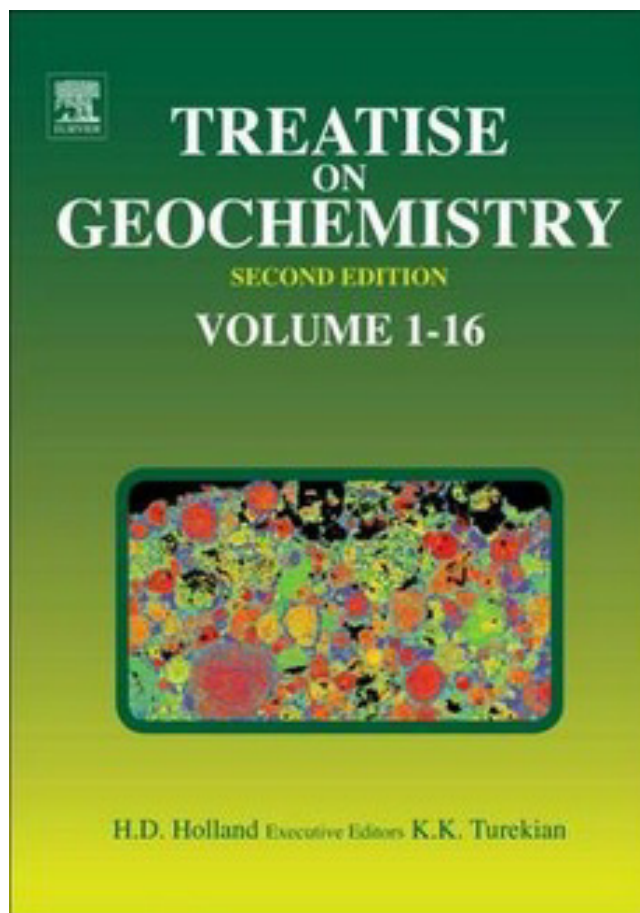


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14.19 Stable Isotopes in Forensics Applications

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14.19.1 Stable Isotope Geochemistry as a Science-Based Forensic Application

14.19.1.1 Overview

Many types of evidentiary material collected during forensic investigations would be familiar to an isotope geochemist; examples include dust accumulated on the bumper of a car, pebbles embedded in shoe treads, or a container of water that was used to create a caustic mixture. One of the main goals of forensic investigations is determining how similar or different seemingly identical pieces of material are, or from where a specimen possibly originated. For instance, a forensic investigator may be interested in knowing if dust on a car bumper matches dust collected from the cuff of a suspect's trousers or where bedrock that could be the source of a pebble is found. As such, the analysis of collected materials for isotopic compositions can be helpful in characterizing specimens based on the elemental record preserved within the material. In this chapter, we discuss the general use and applicability of stable isotope ratio analysis during forensic investigations.

Stable isotope ratio analysis has only relatively recently been utilized in forensic investigations (Benson et al., 2006; Meier-Augenstein, 2010), despite a long history of its application in the biological, ecological, environmental, and geochemical fields (Fry, 2006; Sharp, 2006; West et al., 2006a). The use of stable isotope analysis in forensic investigations is rapidly becoming more commonplace because it results in the addition of a stable isotope fingerprint to the collection of evidence. There exists a suite of elements suitable for stable isotope analysis at natural abundance levels that may be useful for characterizing a specimen of interest. Analyses have traditionally focused on the stable isotope ratios of the relatively abundant elements hydrogen ($\delta^2\text{H}$), carbon ($\delta^{13}\text{C}$), nitrogen ($\delta^{15}\text{N}$), oxygen ($\delta^{18}\text{O}$), and sulfur ($\delta^{34}\text{S}$) though there is utility in the analysis of more rare elements such as lead (Pb) and strontium (Sr) as well. The information gleaned from each element is often unique and, when interpreted in combination, the stable isotope ratios of multiple elements may provide information about a specimen that cannot be acquired using other chemical identification techniques.

Unlike many types of pattern-based evidence collected during a forensic investigation (e.g., bite marks, impressions of tires or footwear, handwriting), stable isotope compositions are quantitative empirical evidence. Stable isotope measurements are repeatable; stable isotope data are reliable, easily validated, and lend themselves well to statistical analyses. These features are often lacking for several types of commonly collected, inferential forensic evidence, according to a review of the forensic science community recently completed by the National Research Council. In 2009, the National Research Council's Committee on Identifying the Needs of the Forensic Sciences Community presented 13 recommendations to address the current challenges faced by the forensic community in the United States at the national, state, and local levels (NRC, 2009). Discussed in more detail at the conclusion of this chapter we note here one salient point of the report: there is a pressing need for a rigorous scientific foundation of the analytical techniques used in forensic investigations. Stable isotope analysis has just such a foundation, developed in the

academic community, and is now poised to make a powerful contribution in the forensic community as well.

14.19.1.2 A Framework for Applying Stable Isotope Analysis in Forensic Investigations

Though not mentioned specifically in the National Research Council's report on the current state of the forensic science community (NRC, 2009), stable isotope analysis can play a significant role in a forensic investigation. This is because the stable isotope fingerprint of a specimen is a unique characterization of the material that can be used to associate samples, glean information on a suspected origin or production method, and infer possible source locations (Ehleringer et al., 2010; Gentile et al., 2011). Specifically, stable isotope measurements can answer three classes of comparative and predictive questions, as presented in Figure 1: (1) How does the isotope fingerprint of the specimen compare to other seized or authentic materials? (2) Is the isotopic composition of the specimen consistent with the prediction for a material originating in a given location? (3) Based on the measured isotopic signature, from where could the specimen have come?

A necessary first step in applying the framework presented in Figure 1 for both comparison and prediction investigations is the creation and population of a database containing measured isotope ratios of authentic samples. This database allows investigators to ask basic questions about similarities among seized samples and between the specimen of interest and previously collected samples. This type of sample matching represents a first-order application of stable isotope analysis in forensic investigations. However, the comparative technique is inherently nonpredictive and nonspatial.

A secondary application of the stable isotope fingerprint of a specimen involves the development of models for prediction. Either simple linear regression models or more complex semi-mechanistic models can be used to describe the isotope effects between the environment, production practice, or biological process and the stable isotope compositions of a material of interest. During an investigation, the modeled mechanisms are used to predict the isotopic composition of a material seized from the same location as the specimen. The models can be built using either authenticated isotopic signatures in the database or some *a priori* knowledge of the mechanisms impacting isotopic compositions. Generally the models also include some estimate of uncertainty, which could be associated to within-sample heterogeneity (natural variation), imprecision of analytical instruments, and/or the variable isotopic effects of sample preparation. During interpretation, the uncertainty estimate is used to supply an assessment of the investigator's confidence in the model predictions.

A third application of stable isotope analysis in forensic investigations is the prediction of potential source or origin using the stable isotope fingerprint of a specimen of interest. This is possible when the mechanisms impacting the stable isotope compositions of a material vary spatially, as when environmental conditions vary across landscapes. In these cases, source inference is possible through the combination of process-based models and the spatial modeling capacity of geographic information systems (GIS). The projection of predicted isotope compositions in a spatial setting creates maps of

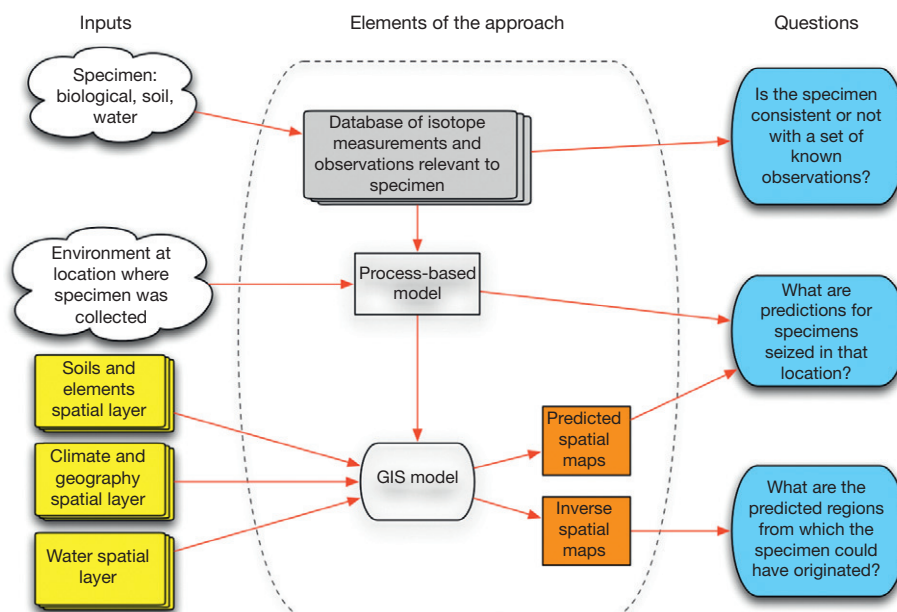


Figure 1 A suggested framework for the application of stable isotope ratio analysis in a forensic investigation. Using this framework, three classes of questions can be answered, as presented on the right: (1) How does the isotope fingerprint of the specimen compare to other seized or authentic materials? (2) Is the isotopic composition of the specimen consistent with the prediction for a material originating in a given location? and (3) Based on the measured isotopic signature, from where could the specimen have come? Note that the last two questions require the development of modeling capabilities; see text for a complete description of this element. Adapted from Ehleringer JR, Thompson AH, Podlesak D, et al. (2010) A framework for the incorporation of isotopes and isoscapes in geospatial forensic investigations. In: West JB, Bowen GJ, Dawson TE, and Tu KP (eds.) *Isoscapes: Understanding Movement, Pattern, and Process on Earth Through Isotope Mapping*. Dordrecht, The Netherlands: Springer, with permission from Springer.

isotope landscapes or *isoscapes*. In the interest of brevity, we refer readers to another text for an additional discussion of the creation and application of isoscapes (West et al., 2010a).

In the remainder of this chapter, we present example forensic applications of stable isotope ratio analysis of a wide variety of nonbiological and biological materials in order to answer questions of varying complexity, from sample comparison to source prediction.

14.19.2 Nonspatial Applications of Stable Isotope Analysis

Arguably the simplest investigative approach utilizing stable isotope fingerprints is comparison of the measured isotopic composition of a collected material to one or more additional specimens. This approach has two forms: comparison of the specimen of interest to other samples collected during the forensic investigation and/or comparison of the specimen of interest to a database of authentic samples. While this application of stable isotope analysis is nonpredictive and nonspatial, it can reveal something of the environmental conditions, material processes, and/or production methods experienced by the specimen. For example, chemically similar samples collected at the same time and from the same location may have experienced similar environmental conditions. If these conditions could alter the isotopic signatures within a specimen, the samples may be isotopically similar and a comparison would reveal those similarities in terms of environmental exposure. The same is true for material processes or production methods.

If the conditions and effects of those conditions on the isotopic compositions of the specimens are well understood, they can be useful in identifying 'like' samples based on a comparison of stable isotope signatures.

14.19.2.1 Synthetic Drugs

Governments and law enforcement agencies have a compelling investigative interest in materials used in criminal activity. This is particularly true for synthetic and semisynthetic drugs of abuse due to the breadth and depth of the production and distribution markets and the size of the organizations often involved. The study of the black-market chemical precursor trade – legitimate chemicals diverted or produced for criminal use – is a developing avenue of investigation for law enforcement and intelligence agencies (Collins et al., 2009; McCusker, 2008; Schneiders et al., 2009). When finished and unfinished drug products, precursors, and recipes are seized, there may be a host of useful forensic evidence contained within the chemicals. For example, the presence or absence of chemical traces (e.g., impurity profiles) can pinpoint a particular production technique, a single laboratory or cook, or even individual batches (Buchanan et al., 2011; Gimeno et al., 2002; Iwata et al., 2008; Kunalan et al., 2009; Manh et al., 2003; Palhol et al., 2002; Waddell Smith, 2007).

Relying heavily on impurity profiles and descriptive/morphological data of drugs and drug precursors has many drawbacks, however, as it is frequently expensive, impractical, and of limited use in source inference. Seized materials often have a long and complex chain of contact, in which each step could

affect the impurity profile and physical description. Vastly varying analysis techniques in use by laboratories may obscure valuable source information in an overload of data generated from these impurity profiles and physical characterizations. Conversely, a highly pure drug seizure may not contain trace chemical evidence that allows discrimination from other highly pure materials (Iwata et al., 2008; Mas et al., 1995). In these cases, the stable isotope ratio analysis of drugs has been recognized as a new and complementary forensic investigative technique (Benson et al., 2006).

14.19.2.1.1 Amphetamine-type stimulants

Amphetamine-type stimulants (ATS) are the second most widely abused drugs after marijuana (*Cannabis*). Synthetic chemicals 3,4-methylenedioxymethamphetamine (MDMA) and methamphetamine are two ATS that have received much attention because of the rising trend of abuse and the discovery of manufacture in global regions previously unaffected (Chawla, 2011). MDMA and methamphetamine have similar avenues of production; both can be produced either from a synthetic intermediate or from natural or semisynthetic (e.g., pseudoephedrine) sources. Due to tighter restrictions on public purchase of pseudoephedrine, such as the nasal decongestant Sudafed®, the production of methamphetamine may be migrating from kitchen-size laboratories to larger laboratories.

Stable isotope ratio studies of MDMA and methamphetamine have traditionally focused on bulk isotope analysis (Carter et al., 2005; Mas et al., 1995). However, recent studies have used compound-specific and site-specific analysis to obtain a more accurate measure of the drug of interest independent of impurities (Carter et al., 2002; Matsumoto et al., 2008; Palhol et al., 2003). When combined with data generated during conventional trace chemical analysis techniques, these isotope analyses can be highly discriminatory, as demonstrated using seizures of street-level MDMA specimens (Buchanan et al., 2011).

The most promising approach for investigating illegal synthetic drugs may be the study of drug precursors and how the precursors' isotopic signals are maintained or modified during the production process. Pseudoephedrine, a direct precursor to methamphetamine, is largely produced by the fermentation of pyruvic acid in the presence of benzaldehyde, followed by reductive amination. Since the reactant pyruvic acid typically comes from sugar produced through C_4 photosynthesis, the $\delta^{13}C$ value of the methamphetamine product is generally more enriched in ^{13}C compared to methamphetamine produced from natural ephedrine, a C_3 plant product. On the other hand, completely synthetic methamphetamine precursors, such as 1-phenyl-2-propanone, are often produced from fossil fuel sources and the carbon isotope ratios of these precursors may be slightly more depleted in ^{13}C than natural ephedrine (Schneiders et al., 2009). It has also been noted that the δ^2H values of pseudoephedrine from synthetic and semisynthetic sources tend to be more depleted than natural ephedrine (Collins et al., 2009; Makino et al., 2007).

The choice of production method for the synthesis of ATS can affect the isotopic signature of the product. When a drug is precipitated from solution, there may be an associated isotopic fractionation (Casale et al., 2005; David et al., 2010). For

instance, studies on MDMA show that reaction routes with many steps produce a product depleted in ^{13}C compared to the precursors (Billault et al., 2007). Likewise, purification of methylamine prior to MDMA or methamphetamine production affects the $\delta^{15}N$ value by producing a product predictably more depleted in ^{15}N than the precursor (Kurashima et al., 2004).

In addition to variations that are due to manufacturing and processing, another major contributing factor to the isotopic signature of a synthetic drug is its precursor. Figure 2 presents dual-isotope plots demonstrating the discriminatory power of multivariate analysis using stable light isotope ratios of the ATS precursor pseudoephedrine. It is possible to discriminate between the five countries of origin of the pseudoephedrine samples using measured δ^2H , $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$ values.

14.19.2.1.2 Performance-enhancing steroids

The use and abuse of performance-enhancing anabolic steroids is an unfortunate reality in modern-day sports (Cawley and Flenker, 2008). The World Anti-Doping Agency (WADA, <http://www.wada-ama.org/>) was created in 1999 to combat the practice of doping in both professional and amateur sports. Dedicated to coordinating education with research and working to develop new methods to detect steroid use in athletes, WADA also works closely with the International Olympic Committee to monitor the potential misuse of drugs by Olympic athletes (Hemmersbach, 2008).

Traditionally, doping detection was based upon the ratio of testosterone (T) to epitestosterone (E) within the urine, as measured by gas chromatography–mass spectrometry (GC–MS); a T/E value >6 was defined as evidence of doping with testosterone (Aguilera et al., 1996; Shackleton et al., 1997). Yet GC–MS techniques are limited to only the identification and quantification of steroids because the chemical structures of synthetic and natural steroids are identical. For this reason, GC–MS analysis alone cannot distinguish exogenously administered testosterone from that produced endogenously within the athlete's body (Cawley and Flenker, 2008). In addition, quantification techniques like GC–MS may not be useful in cases where both exogenous T and E were administered, which would have little to no effect on the T/E ratio, or when an athlete's baseline T/E ratio is naturally elevated.

The compound-specific carbon isotope ratio measurement of steroids via GC–combustion–isotope ratio MS (GC–C–IRMS) can detect doping in instances where T/E ratios appear normal. This is because the source of synthetic testosterone is typically a C_3 plant (soy) and is therefore characterized by relatively low $\delta^{13}C$ values (approximately -30% ; Shackleton et al., 1997). In contrast, the $\delta^{13}C$ value of natural testosterone will reflect that of the athlete's diet (Aguilera et al., 1996; Shackleton et al., 1997), which typically contains both C_3 and C_4 plants and so is characterized by values of approximately -27% to -20% (though some South African subjects have been found to have higher natural testosterone $\delta^{13}C$ values of -17% ; Aguilera et al., 1996). Even without prior knowledge of the carbon isotopic composition of an athlete's dietary inputs it is possible to detect exogenous testosterone doping because the $\delta^{13}C$ values of natural testosterone precursors (e.g., endogenous reference compounds; Shackleton et al., 1997) will not change after exogenous T administration,

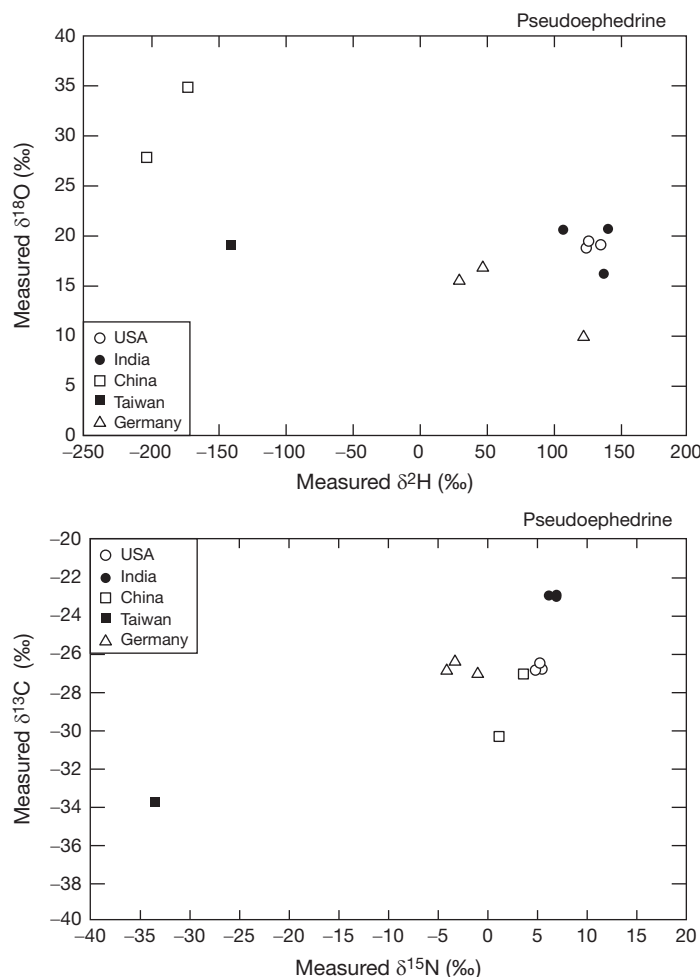


Figure 2 Dual-isotope plots (oxygen vs. hydrogen, top; and carbon vs. nitrogen, bottom) of known-origin pseudoephedrines from five countries. The combination of four isotope ratios measured for each sample is sufficient to determine country of origin.

while the $\delta^{13}\text{C}$ values of testosterone metabolites will change (Becchi et al., 1994).

These GC–C–IRMS techniques also have application for detecting illegal drug administration in racehorses and other livestock. Aguilera et al. (1997) demonstrated that the measured $\delta^{13}\text{C}$ values of exogenous and endogenous hydrocortisone from horse urine are different, thereby allowing investigators to detect the illegal doping of racehorses with corticosteroids to manage pain and inflammation (Aguilera et al., 1997). The illegal use of testosterone to promote growth in beef cattle can also be detected via GC–C–IRMS (Ferchaud et al., 1998).

14.19.2.2 Manufactured Explosives

The stable isotope composition of an explosive material (trinitrotoluene) in a forensic investigation was first published in 1975 (Nissenbaum, 1975). Since that time, continued work has demonstrated that IRMS is a useful analytical technique to chemically distinguish explosive materials, residues, and precursors (Barnette et al., 2011; Benson et al., 2006; Lock and Meier-Augenstein, 2008; McGuire et al., 1993). It is often difficult to link recovered manufactured chemicals of high

purity from a crime scene to other related specimens or to a potential source, as these materials typically have virtually identical physical and chemical properties. This is particularly true for commercial and military explosives, as the chemical makeup is closely controlled. To trace an unexploded bomb or explosion residue to a manufacturer, the use of chemical tracers or markers (i.e., taggants) mixed into the explosive material has been suggested, but this solution has legal, cost, and chemical compatibility problems (CPSMA and DEPS, 1998). In the absence of markers like taggants, investigators must look for other traceable evidence, such as stable isotope signatures, to link a suspect to a crime scene.

14.19.2.2.1 Peroxide-based explosives

Organic peroxides can be used to manufacture explosives, such as triacetone triperoxide (TATP), hexamethylene triperoxide diamine (HMTD), and simple mixtures containing H_2O_2 and a carbon source. Peroxide-based explosives are extremely sensitive to shock, heat, and friction and have no commercial or military applications (Schulte-Ladbeck et al., 2002). However, the materials used in their manufacture are readily available household chemicals and these explosives are relatively easy to produce; as such, peroxide-based explosives are attractive to

terrorist groups (Benson et al., 2009b). For example, a TATP booster was used in the 1994 Israeli Embassy Bombing in London (Benson et al., 2009b; Naughton, 2005) and in 2001 Richard Reid was charged with attempting to use a TATP-initiated explosive aboard an American Airlines flight (Oxley and Smith, 2006). TATP was used in the July 2005 London transportation bombings (Meier-Augenstein, 2010) and in 2006 there was an attempt to carry homemade explosive devices, allegedly containing TATP, aboard a transatlantic flight between the United Kingdom and the United States (Benson et al., 2009b; CNN.com., 2010). More recently, in 2009, there was an alleged attempt by extremists to detonate peroxide-based explosives on the New York City subway system (FBI, 2009).

There has been a significant amount of research dedicated to the identification of peroxide-based explosives and postblast residues. Tested techniques include liquid chromatography–MS (Crowson and Beardah, 2001), GC–MS (Muller et al., 2004; Sigman et al., 2006; Stambouli et al., 2004), infrared spectroscopy (Buttigieg et al., 2003), and desorption electrospray ionization (Cotte-Rodríguez et al., 2006; Schulte-Ladbeck et al., 2002). What all these identification methods lack, however, is the ability to distinguish between two chemically identical specimens something that stable isotope analysis can provide (Lock and Meier-Augenstein, 2008).

To demonstrate the distinguishing power of stable isotope signatures, Lock and Meier-Augenstein showed hexamine, a precursor for HMTD, from several suppliers had unique carbon and nitrogen isotope values where the measured ranges of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values for the hexamines were approximately 12 and 3‰, respectively (Lock and Meier-Augenstein, 2008). Lock et al. (2010) demonstrated a strong isotopic link during laboratory synthesis between hexamine and HMTD for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^2\text{H}$ values suggesting the discriminatory power of these isotope signatures is retained through the production process (Lock et al., 2010). Samples of TATP were uniquely distinguishable by both $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values, with a reported total range of 20‰ for both, as well as a 12‰ range in $\delta^{18}\text{O}$ values (Benson et al., 2009b). Studies on hydrogen peroxide, a reagent in peroxide-based explosive manufacture, found large ranges in $\delta^2\text{H}$ (230‰) and $\delta^{18}\text{O}$ (24‰) values of commercial hydrogen peroxide solutions, as well as in the $\delta^{18}\text{O}$ values (11‰) of hydrogen peroxide (Barnette et al., 2011; Lock, 2009). Currently, there are limited published isotope data for the reagent acetone, which is used in the synthesis of TATP (Huang et al., 1999). Unpublished work by J. Barnette and colleagues shows a large range in $\delta^{13}\text{C}$ (11‰), $\delta^2\text{H}$ (113‰), and $\delta^{18}\text{O}$ (22‰) isotope values of commercially available acetone from beauty supply, hardware, and scientific supply stores. Together, these investigations demonstrate that both HMTD and TATP specimens and the reagents used to manufacture peroxide-based explosives can have unique isotope signatures, especially when combining isotope ratio data from more than one element, which may ultimately be used to assist law enforcement agencies in criminal investigations.

14.19.2.2.2 An industrial explosive: ammonium nitrate

Though not an explosive under normal circumstances, the widely used fertilizer ammonium nitrate (AN, NH_4NO_3) is considered an explosive ingredient and its storage and

transportation are highly regulated (CPSMA and DEPS, 1998; Kaye and Herman, 1978). AN has been used since the beginning of the twentieth century in explosives, and its dangers are well-known from the Texas City disaster of 1947 that killed at least 581 people (Stephens, 1997), multiple bombing campaigns by the Irish Republican Army (Benson et al., 2009a), and – more recently – the Oklahoma City bombing of 1995 (Giordano, 2003). In 1995, antigovernment domestic terrorist Timothy McVeigh used 4800 pounds of AN/nitromethane mixture, AN/fuel oil mixture, and Tovex (a water-gel explosive also based on AN) to collapse most of the Alfred P. Murrah Federal Building in Oklahoma City, Oklahoma, USA, killing 168 people and injuring an additional 680. AN has also been used in terrorist bombings in Asia and the Middle East (Swami, 2011) as well as in improvised explosives in Afghanistan (Brummitt, 2011; Rodriguez, 2010).

Tracking the transfer of AN from large, centralized factories through various intermediaries to criminal end use is a daunting task and sourcing regulation has been slow or nonexistent. In countries such as Pakistan there are no means of tracking AN even by the packaging materials (Brummitt, 2011). Stable isotopes may be a tool in tracking the movement of AN, but the variability of the isotopic fingerprint of AN from various sources must first be understood.

AN is synthesized from the reagents ammonia and nitric acid, both of which contribute N atoms to the product. The source of N for ammonia and nitric acid is the atmosphere, which has a defined $\delta^{15}\text{N}$ value of 0‰. If we assume there is a high yield or little waste during the manufacturing process, we would thus expect the $\delta^{15}\text{N}$ values of AN to be near that of atmospheric N_2 . We expect variation in AN $\delta^{15}\text{N}$ values only when: (1) there is low yield and subsequent purging of reactants during production; (2) there is an excess of a particular reactant; and/or (3) the ammonia or the nitric acid reagents are from a nonatmospheric source. Similarly, the majority of O atoms in AN come from nitric acid and ultimately originated from atmospheric O_2 , which has a relatively constant $\delta^{18}\text{O}$ value of $\sim 23.5\text{‰}$ (Kroopnick and Craig, 1972). Thus, we would expect the $\delta^{18}\text{O}$ values of AN to deviate from 23.5‰ only when reaction conditions vary as described above for $\delta^{15}\text{N}$ values.

Previous studies of the nitrogen isotope ratios of AN fertilizers showed a range that spanned -8 to $+7\text{‰}$, with the vast majority between -2 and $+2\text{‰}$ (Macko and Ostrom, 1994). Benson and colleagues reported nitrogen isotope variation in AN from three manufacturers in Australia; they also reported measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of AN samples from four additional countries (Benson et al., 2009a). They found significant variation in the nitrogen isotope ratios of samples over time from one of the Australian manufacturers, and varying isotope ranges from each of the sampled countries. There were no clear groupings that discriminated Australian AN sources from other sources, as the ranges for the measured isotope ratios overlapped.

Focusing on high-purity AN samples of both explosives and fertilizer grade, we measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values for 42 AN specimens taken from six different countries and from at least nine different manufacturers within the United States (Figure 3). The upper and lower 95% confidence intervals for $\delta^{15}\text{N}$ values are -0.8 and -1.4‰ , respectively, with a mean

of -1.1‰ . The upper and lower 95% confidence intervals for $\delta^{18}\text{O}$ values are 20.1 and 18.9‰, respectively, with a mean of 19.5‰. The specimens represented both fertilizer- and explosives-grade AN. As is evident in Figure 3, all samples were depleted in ^{18}O relative to atmospheric O_2 , and all but two were depleted in ^{15}N relative to atmospheric N_2 .

14.19.2.2.3 A military-grade explosive: pentaerythritol tetranitrate

Pentaerythritol tetranitrate (PETN) is the main component in many commercial and military explosives. PETN is attractive for terrorist use, as it is one of the most powerful explosives available and is sensitive enough for blasting caps and detonation cords, but very stable and relatively safe to use (Meyer et al., 2002). It can be used either as a powder or mixed with phlegmatizing materials to form shaped charges, such as the plastic explosive Semtex (Moore et al., 2010). PETN has been involved in several high-profile bombing incidents including the Pan Am 103 'Lockerbie' bombing in 1988 and the 'Shoe Bomber' bombing attempt in 2001, among others (Belluck and Chang, 2001; SSCI, 2010; Swami, 2011).

Carbon, hydrogen, nitrogen, and oxygen are the only elements in PETN (Figure 4). Under normal laboratory conditions, there are no labile atoms, and therefore the stable isotope signature is preserved despite exposure to air, light, moisture, and dissolving organic solvents such as acetone and acetonitrile (J. Howa and M. Lott, unpublished data). The discriminatory power of the isotope ratio signature of a mixed explosive material, such as Semtex, relies heavily on

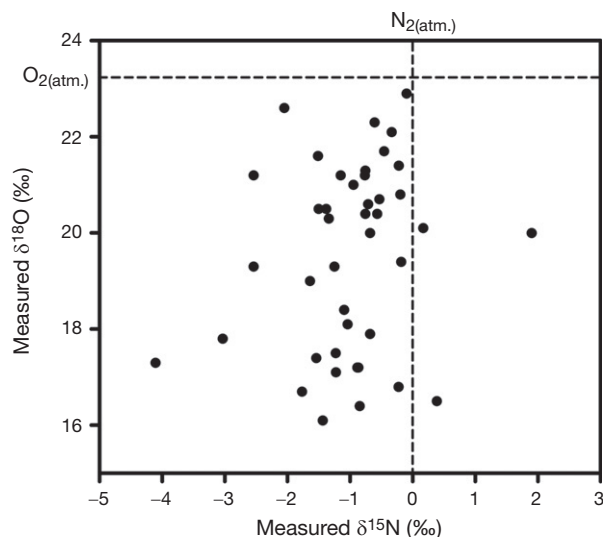


Figure 3 Measured nitrogen and oxygen isotope ratios of 42 ammonium nitrate specimens. Samples were collected from six countries and at least nine manufacturers. Shown for comparison is the defined value of atmospheric N_2 ($\delta^{15}\text{N} = 0\text{‰}$) and average value of atmospheric O_2 ($\delta^{18}\text{O} = +23.5\text{‰}$; Kroopnick and Craig, 1972).

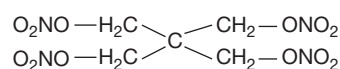


Figure 4 Molecular structure of pentaerythritol tetranitrate (PETN).

the strength of databases of authentic material. Most previous isotope studies of PETN have reported only bulk carbon and nitrogen stable isotope ratios (Pierrini et al., 2007), making databases of limited utility due to the wide variety and heterogeneity of mixed explosive materials. However, compound-specific isotope analysis has allowed for the analysis of individual explosive components while simultaneously reducing the overall isotopic heterogeneity seen in mixed explosives.

To address precision and accuracy in the analysis of the PETN component of mixed explosives, we followed the principle of identical treatment using a pure PETN specimen obtained from a factory, similar to the sample material under investigation (Brand, 2009). Calibrated values were $\delta^{15}\text{N}_{\text{PETN}} = -14.27 \pm 0.74\text{‰}$ (standard deviation (1σ), $n = 38$) relative to atmospheric nitrogen and $\delta^{13}\text{C}_{\text{PETN}} = -38.19 \pm 0.26\text{‰}$ (1σ , $n = 38$) relative to VPDB (via the method of Coplen et al. (2006)). Using these statistics to estimate the error of the analysis method, we assert that when:

$$\left| \frac{\delta_{\text{specimen}} - \delta_{\text{group}}}{\sigma_{(\delta)}} \right| > 1.96$$

the measured isotope ratio of any specimen of interest would lie outside the 95% confidence limit for a group. Therefore, a specimen that has a distance from a group of $|\delta^{15}\text{N}_{\text{specimen}} - \delta^{15}\text{N}_{\text{group}}| > 0.74\text{‰} \times 1.96 = 1.45\text{‰}$ for nitrogen and/or $|\delta^{13}\text{C}_{\text{specimen}} - \delta^{13}\text{C}_{\text{group}}| > 0.26\text{‰} \times 1.96 = 0.52\text{‰}$ for carbon would be considered from a different source or origin.

A plot of the measured $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of the PETN component of 146 mixed explosive specimens is presented in Figure 5. The figure includes samples we acquired from factories, explosives of a known origin, and field-recovered specimens. Because the samples span large isotopic ranges ($\sim 60\text{‰}$ for $\delta^{15}\text{N}$ and $\sim 25\text{‰}$ for $\delta^{13}\text{C}$ values) and because many groups of samples have known origin, it is highly likely that a random

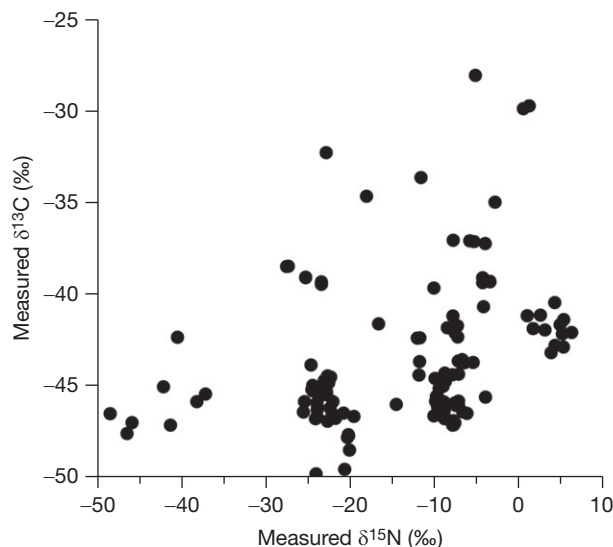


Figure 5 Measured carbon and nitrogen isotope ratios of the PETN component separated from 146 mixed explosive specimens. Samples include factory acquisitions, explosives of known origin, and field-recovered specimens.

PETN specimen could be matched with a known-origin PETN group if the isotopic compositions of specimen were within the limits of the group, as defined above.

14.19.2.3 Packaging Materials

Seizures of illicit drugs or explosives often result in the collection of additional forensic evidence, including materials used for packaging such as plastic bags, plastic wrappings, and adhesive tape. There are a host of traditional techniques used for examining these collected materials (e.g., visual observation, spectroscopic techniques, chemical composition analysis; Horacek et al., 2008). Recently stable isotope analysis has been applied more and more frequently to the examination of seized packaging material. The preparation of packaging materials for stable isotope analysis is relatively straightforward and requires little material (~100–200 µg), which is appealing in instances of small samples like those often collected as evidence during forensic investigations.

Measured carbon and hydrogen isotope ratios have been successfully used to discriminate different brands of brown packaging tape collected in both the United Kingdom (Carter et al., 2004) and Korea (Horacek et al., 2008). Work by Horacek et al. (2008) indicated that rolls of tape are generally isotopically homogeneous, suggesting that multiple pieces of tape from a single roll should be relatable via stable isotope compositions. In addition to measuring bulk stable isotope ratios of intact tape samples for comparison purposes, Carter et al. (2004) have also suggested following a guided analytical protocol for separating the tape adhesive (glue) from the plastic-based backing and analyzing the separate components for $\delta^{13}\text{C}$, $\delta^2\text{H}$, and finally $\delta^{18}\text{O}$ values until it is possible to conclusively differentiate (or not) two tape samples. Measured carbon and hydrogen isotope ratios are similarly useful in differentiating samples of other plastic-based packaging materials, such as plastic zip-top bags (Taylor et al., 2008) and cling films (Idoine et al., 2005).

14.19.2.4 Crude Oils and Petroleum Products

Forensic applications of the stable isotope analysis of crude oils and petroleum products are broad in range and include source rock identification, oil spill source investigation, and export/import control. While gas chromatographic techniques are useful to determine the distribution of compounds within crude oils, isotope analysis of the bulk oil and its individual compounds can provide additional information to characterize particular oils and source rocks (Peters et al., 2005). Stable isotope analysis is particularly valuable in spill scenarios where many of the diagnostic molecular components of petroleum products can be rapidly lost to the surrounding environment (Wang and Fingas, 2003), as environmental alteration does not markedly alter the isotope ratios of the remaining materials (Hartman and Hammond, 1981; Macko et al., 1981; Mansuy et al., 1997; Sun et al., 2005).

The isotope signatures of bulk and individual petroleum hydrocarbons are determined by the isotopic composition of the organic source materials and fractionations that occurred during and after petroleum genesis (Fux, 1977) with carbon, hydrogen, sulfur, and nitrogen being the elements most

commonly analyzed. One of the first forensic applications of stable isotope analysis related to environmental contamination focused on a petrochemical plant's inflow and outflow waters (Calder and Parker, 1968). Calder and Parker (1968) found the carbon isotope ratios of dissolved and particulate material in the outflow waters were depleted in ^{13}C by more than 9‰ more than in the inflow waters, suggesting an added contribution of isotopically depleted petrochemicals to the outflow.

Isotope analysis was also used in a forensic context during the high-profile *Exxon Valdez* oil spill in 1989. Following the spill, collected tar ball and oil residues from Prince William Sound, Alaska, USA, were used to assess clean-up effectiveness (Kvenvolden et al., 1993). Bulk carbon isotopic analysis of collected materials indicated two populations of isotope values, one corresponding to oil spilled from the *Valdez* and the other reflecting imported Californian petroleum products derived from the Monterey Formation (Kvenvolden et al., 1995). The authors suggested the source of the Monterey Formation oil was stored petroleum products spilled in the Prince William Sound during the Great Alaskan Earthquake of 1964. To support this argument, the authors documented widespread use of Californian petroleum products in Alaska prior to the development of Alaskan North Slope oil fields, and demonstrated that these products had isotopic values that matched the tar balls found (Kvenvolden et al., 1998).

The recent advent and widespread application of compound-specific isotope analysis of H, C, N, O, and even S, has allowed additional forensic questions to be addressed regarding petroleum contamination and spills. The application of stable isotopes to oil spill forensics and other environmental forensic applications have been reviewed in detail by Philips (2002), Peters et al. (2005), and Jeffrey (2007). We foresee that these techniques will be applied to forensic questions regarding oil spills and environmental contamination with increasing regularity.

14.19.3 Spatial Applications of Stable Isotope Analysis

The examples offered thus far have shown how variation in reactants, chemical pathways, and reaction conditions can lead to variation in the stable isotopic composition of evidentiary materials. In some instances these differences may be largely independent of spatial environmental factors, as when the efficiency of production in specific factories governs the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of AN (see Section 14.19.2.2.2). In many cases, however, the isotopic compositions of materials exhibit strong, predictable variation as a function of local environmental conditions. The most common examples involve materials from natural biological or geological systems where reactions take place under environmentally influenced conditions. The environmental influence can also extend to highly controlled manufacturing processes, as when the isotopic composition of locally derived chemical substrates, such as water, contributes to the isotopic signature of a product. By linking to databases and models describing the distribution of isotopes in environmental substrates and the variation in isotopic fractionation under different conditions, we can begin to build a predictive

framework relating the isotopic composition of forensic evidence to location (see [Figure 1](#)). This framework often involves the development of predictive isoscapes for biological and man-made products, which represent the combined influence of local substrates (water, bedrock geology, CO₂, food, etc.) and local conditions (temperature, hydroclimate, land use, demography, etc.) on isotopic values for materials produced at different sites. Depending on the system and application in question, these isoscapes are developed using empirical transfer functions, process-based models, or some combination thereof, and are informed by a diverse array of geospatial data products.

14.19.3.1 Water Isotopes and the Isoscapes Foundational Approach

Isotope effects associated with evaporation and condensation fractionate H and O isotopes as they move through the hydrological cycle, producing strong, systematic patterns of water isotope variation in continental waters. This variation has been documented by the International Atomic Energy Agency's Global Network of Isotopes in Precipitation over the past 50 years ([Rozanski et al., 1993](#)), and these data are now complemented by observations from a large number of regional networks and investigator-driven programs (e.g., [Gibson et al., 2005](#); [Longinelli and Selmo, 2003](#); [Welker, 2000](#)). The dominant patterns of variation in continental water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were characterized decades ago, and include decreases in the relative abundance of the heavy isotopes in water at high latitude, high altitude, and in the continental interiors ([Craig, 1961](#); [Dansgaard, 1954, 1964](#)). These patterns are driven by the progressive loss of moisture from air masses as they cool and produce precipitation, which preferentially removes ^2H and ^{18}O , leaving the residual vapor, and any subsequent precipitation formed from it, depleted in these isotopes. In addition, strong seasonal variation in precipitation isotope ratios is observed in most environments with strong climatic seasonality, and can be attributed to the effects of seasonal temperature change and/or precipitation intensity on the extent of rainout from air masses in different regions of the world ([Alley and Cuffey, 2001](#); [Bowen, 2008](#); [Rozanski et al., 1993](#)).

A large body of theory has focused on describing the isotope effects associated with rainout and evaporation processes ([Craig and Gordon, 1965](#); [Gat, 1996](#)), providing a mechanistic framework for linking water isotope variation to spatially varying environmental factors such as temperature, elevation, and relative humidity. A number of authors have capitalized on these relationships to develop precipitation water isoscapes using statistical or geostatistical models parameterized with variables that are correlated with the process of rainout and, therefore, precipitation $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values ([Bowen, 2010b](#)). Several parameterizations have been explored using global and regional gridded environmental data, and have shown considerable power to describe precipitation isotope ratios as a function of variables such as temperature, latitude, and altitude ([Bowen, 2010a](#)). In almost all cases, the residual variance not explained by the models exhibits significant spatial autocorrelation ([Bowen and Wilkinson, 2002](#); [Bowen et al., 2005b](#); [van der Veer et al., 2009](#)), suggesting that the parameters used are inadequate to completely describe the environmentally driven

spatial variation in precipitation isotope ratios. Following on the work of [Bowen and Wilkinson \(2002\)](#) many studies now incorporate regional adjustments to the statistical model output based on geostatistical interpolation of model residuals. The resulting isoscapes are able to predict long-term average (climatological) precipitation isotope ratios at unmonitored sites with an average error of <10‰ for $\delta^2\text{H}$ and <1.2‰ for $\delta^{18}\text{O}$ values ([Bowen and Revenaugh, 2003](#)).

As precipitation-derived water propagates through the hydrological cycle it largely preserves its isotopic composition, and a growing body of work has documented the spatial relationships between precipitation and other water resources that are often more directly relevant to forensic investigations. Rivers, lakes, and groundwater are the dominant sources of water used in irrigation, industrial processes, and domestic water supplies, with surface water sources supplying 42, 80, and 63% of the water used in these categories, respectively, in the United States during the year 2000 ([Hutson et al., 2004](#)). Systematic documentation of the large-scale spatial variation in surface water isotopic composition is not available for most regions, although several short-term projects have generated useful datasets (e.g., [Gibson and Edwards, 2002](#); [Henderson and Shuman, 2009](#); [Kendall and Coplen, 2001](#)). Analysis of these data in the context of precipitation isoscapes has demonstrated the strong first-order control that spatial patterns of precipitation $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values exert on continental freshwater systems ([Bowen et al., 2011](#); [Dutton et al., 2005](#); [Gibson and Edwards, 2002](#); [Henderson and Shuman, 2009](#)). In each case, systematic regional deviations between precipitation and surface water data were found and have been attributed to factors including lateral transport of water in river systems, seasonal imbalances in the partitioning of precipitation between runoff and evapotranspiration, and isotope effects associated with evaporation from soils and surface water bodies. Work with process-based spatial hydrology models ([Bowen et al., 2011](#); [Fekete et al., 2006](#); [Gibson et al., 2010](#)) has shown that regional- to continental-scale patterns in long-term average surface water isotope ratios can be simulated reasonably accurately (root mean square error $\approx 8\%$ for $\delta^2\text{H}$ and 1.1‰ for $\delta^{18}\text{O}$; [Bowen et al., 2011](#)) if driven by accurate maps of precipitation isotope ratios and environmental variables such as precipitation and evapotranspiration amounts. Regional studies of fresh groundwater have typically shown that values from subsurface reservoirs are similar to those of local precipitation, but systematic deviations have been demonstrated where (1) groundwater is derived from ancient (thousands to millions of years old) precipitation ([Kay et al., 2002](#); [Rozanski, 1985](#); [Smith et al., 2002](#); [Sultan et al., 2000](#)); (2) groundwater recharge is dominated by precipitation from high-elevation sources in mountainous terrains ([Manning and Solomon, 2003](#); [Scholl et al., 1996](#)); or (3) artificial recharge from imported water constitutes a large fraction of aquifer water ([Clark et al., 2004](#); [Coplen et al., 1999](#)).

Spatial isotope ratio variation is propagated to waters extracted from these sources, as documented in published surveys of tap water isotope ratios ([Bowen et al., 2007b, 2011](#); [Kennedy et al., 2011](#)). In local or regional case studies, analysis of extracted waters can elucidate the origin of water used in public supply systems, agriculture, and industry, with potential forensic applications in water management and

rights enforcement (Bowen et al., 2007a; Guay et al., 2006) and product authentication (see Sections 14.19.3.2 and 14.19.4.1). Tap water isoscapes have also been produced for limited regions of the continents by combining precipitation isoscapes with geospatial analysis of residuals from tap water/precipitation comparisons at monitoring sites (Bowen et al., 2007b), and provide a generalized template for interpreting data from water and water-derived materials originating from anthropogenic systems. Although the quality of these data products remains highly dependent upon the availability of tap water isotope databases, potential exists to improve them through the development of better parameterized models representing isotope effects associated with natural and human-modified hydrological processes (Bowen et al., 2011).

Water isoscapes are widely applicable in forensic and non-forensic applications, and routine methods now exist to produce reasonably accurate isoscapes for many hydrological systems. The production and documentation of these products is achievable using GIS or other modeling software. Nevertheless, the generation of reliable gridded environmental datasets remains a nontrivial challenge, and variation in the data and methods used can have a substantial impact on the accuracy and precision of predicted spatial isotope distributions (Bowen, 2010b). In order to support the widespread application of isoscapes by a diverse user base, many well-documented water isoscapes are now freely distributed via the web through WaterIsotopes.org (<http://waterisotopes.org>). In addition, a next-generation tool for water isotope mapping, IsoMAP (<http://isomap.org>), was recently released. This resource provides access to databases and statistical and process-based models that allow user-driven development of new isoscapes through a web-browser interface (Lee et al., 2011). Details of the modeling process, data, and methods are automatically documented by the IsoMAP system, meaning that IsoMAP allows the development of highly customized isoscapes for specific applications and that the resulting data products are well documented and traceable.

14.19.3.2 Waters, Beverages, and the Isoscapes Potential

As described above, spatially variable environmental factors such as temperature and elevation can impact the isotopic composition of precipitation and tap waters and thus impact the isotopic composition of water-based beverages. The expected link between local source conditions and water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values has been previously documented for bottled waters from across the globe (Bong et al., 2009; Bowen et al., 2005c; Brencic and Vreca, 2006). Reviewing one publication in particular, Bowen et al. (2005c) found that the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of bottled waters generally matched the normal range of meteoric waters in the purchase locations and suggested that the stable isotope ratios of bottled waters might therefore be useful to monitor the potential misuse of local water resources and to understand the transport of bottled water from origin to consumer. As an extension to this work, Chesson and colleagues investigated the possible source of water in several commonly imbibed, water-based beverages available for purchase within the United States using stable isotope analysis (Chesson et al., 2010b,c). They found that the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of beverages distributed at local scales (e.g., carbonated soft drinks) matched the isotopic

composition of the consumers' local tap water more closely than beverages distributed at regional scales (e.g., beer and milk).

The stable isotope analysis of water within beverages is useful to characterize one of the largest components of daily human intake, which directly impacts the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the body water pool. In order to use hydrogen and oxygen isotope ratios to investigate the origin and movement of humans (see also Sections 14.19.5.2 and 14.19.5.3), it is important for modelers to understand how closely linked the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of imbibed beverages are to locally available water. If hair from a subject that is known to drink large quantities of prepared beverages is collected and analyzed, a researcher would be interested in understanding the relationship between the isotopic composition of local tap water and beverages prepared from that water. To investigate this question for one particular drink category – caffeinated beverages brewed with heat – we collected a series of freshly made coffees and teas from food establishments in Salt Lake City, Utah, USA alongside samples of the tap water (source water) used to make those drinks. Water from the brewed beverages was cryogenically extracted prior to stable isotope analysis (West et al., 2006b). We found that the brewing process had relatively little isotopic effect on measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, with an average difference between the source water and extracted beverage water of $-3 \pm 3\text{‰}$ and $-0.5 \pm 0.6\text{‰}$, respectively (Table 1).

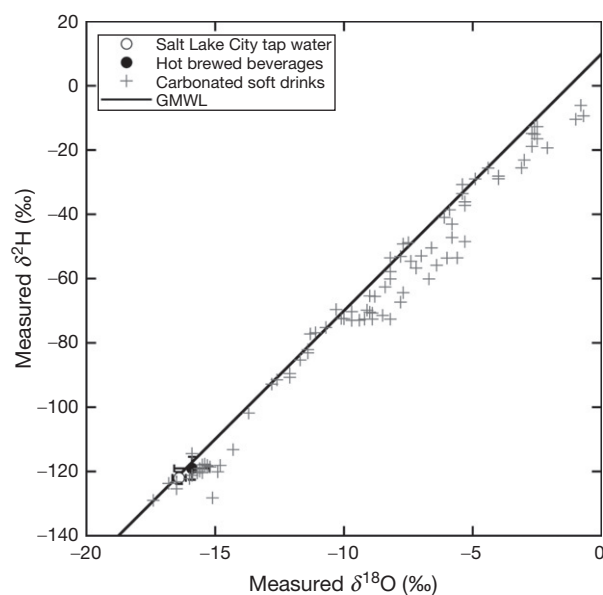
Displaying beverage data on dual-isotope cross-plot reveals further evidence for the link between beverage water and source water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. Shown in Figure 6 is a collection of carbonated bottled or canned colas (primarily Coca-Cola® Classic) purchased from across the United States, alongside the average $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the tap waters and brewed caffeinated beverages collected in Salt Lake City, Utah, USA (Table 1). The relationship between the hydrogen and oxygen isotope ratios of these caffeinated beverages mimics the Global Meteoric Water Line (GMWL; $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10\text{‰}$; Craig, 1961). While we do not know the original source of water used to make many of the colas presented in Figure 6, it appears the processes used in the production of both hot and cold caffeinated beverages do not significantly fractionate against ^2H or ^{18}O , as evidenced by the agreement between measured beverage water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values and meteoric waters represented by the GMWL. Fractionation caused by evaporative processes during beverage production would generate $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ covariation with a slope lower than that of the GMWL (Gat, 1996). In the case of hair collected from a coffee- or cola-guzzling subject, an investigator can therefore assume meteoric water isotopic compositions are a good proxy for the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the imbibed beverages that were recorded by the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the amino acids in the hair keratin.

Caffeinated beverages produced in coffee houses and bottling plants are not the only beverages to display significant covariation in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. Using a survey of milk from across the United States, Chesson et al. (2010b) found that the hydrogen and oxygen isotopic compositions of water extracted from milk samples were strongly and linearly correlated. The authors suggested this covariation was evidence that milk water records the stable isotope ratios of drinking

Table 1 Comparison of measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of paired tap ('source') water samples and water extracted from various brewed caffeinated beverages collected in Salt Lake City, Utah, USA

Establishment	Product	Tap water (‰)		Brewed product ^a (‰)		Difference (Δ , ‰)	
		$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$
Aristo's	Coffee	-124	-16.7	-120	-15.9	-4	-0.8
Café Med	Coffee	-121	-16.2	-121	-16.2	0	0.0
Denny's	Coffee	-120	-16.1	-118	-15.6	-2	-0.5
Greek Town	Coffee	-122	-16.4	-121	-16.5	0	0.1
Greenhouse Effect	Coffee	-123	-16.7	-122	-16.6	-1	0.0
Home coffee maker	Coffee	-119	-16.1	-116	-15.3	-4	-0.8
Salt Lake Roasting Co.	Coffee	-123	-16.6	-122	-16.3	-1	-0.3
Seven-11	Coffee	-123	-16.6	-122	-16.0	-1	-0.6
Starbuck's	Coffee	-118	-16.3	-119	-16.1	0	-0.1
Greenhouse Effect	Espresso	-123	-16.7	-119	-16.6	-4	-0.1
Salt Lake Roasting Co.	Espresso	-123	-16.6	-113	-16.2	-10	-0.3
Starbuck's	Espresso	-118	-16.3	-112	-15.8	-7	-0.4
Kyoto	Green tea	-123	-16.3	-120	-16.1	-3	-0.3
Mikado	Green tea	-125	-16.8	-122	-16.3	-3	-0.5
Tachibana	Green tea	-121	-16.3	-122	-16.6	1	0.3
Chick-fil-A	Sweet tea	-120	-16.1	-120	-15.8	1	-0.3
Famous Dave's	Sweet tea	-120	-16.2	-116	-15.6	-4	-0.7
Mediterranean Café	Tea	-120	-15.9	-111	-13.8	-9	-2.2
Salt Lake Roasting Co.	Tea	-123	-16.6	-116	-14.9	-7	-1.7
Mean		-122	-16.4	-119	-15.9	-3	-0.5
Standard deviation		1.9	0.26	3.6	0.69	3.2	0.60

^aWater cryogenically extracted from brewed product for stable isotope analysis.

**Figure 6** Measured hydrogen and oxygen isotope ratios of water from various caffeinated beverages. The Global Meteoric Water Line (GMWL; $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10\text{‰}$; Craig, 1961) is shown for comparison.

water available to the dairy cows. A subset of paired milk and drinking water samples supported this hypothesis. The relationships between the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of milk water and cow drinking water were significant and generally fit 1:1 lines, albeit with an increase in isotopic values from tap to milk related to the input of H and O atoms into milk water from sources other than drinking water (e.g., feed, atmospheric O_2).

Using the regression line describing the dependence of milk water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values on cow drinking water (Chesson et al., 2010b), it is possible to apply the model in an inverse fashion to predict drinking water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values from the analysis of water extracted from a milk of unknown origin (Chesson et al., 2011a), thereby learning something of the potential origin of the investigated sample. This work has several applications, including tracing the sources and distributions of tainted milk shipments. The use of stable isotope analysis as it directly applies to food origin authentication is discussed in more detail in Section 14.19.4.2.

14.19.4 Plant-Related Forensic Applications of Stable Isotope Analysis

14.19.4.1 Economic Adulteration of Foods

The adulteration of foodstuffs can fit many forms, including the omission of a valuable component or substitution of one valuable component with another of inferior quality (e.g., replacement of cocoa butter with vegetable fats; Gomstyn, 2008); the deliberate concealment of defects or damage; and the addition of substances to increase mass or reduce quality (e.g., injecting scallops with water; Anonymous, 2002). Food items can also be deliberately or unintentionally mislabeled as to origin, appellation, or production. Almost all forms of adulteration and misidentification are economically motivated and are prompted in part by the willingness of consumers to pay premium prices for certain foodstuffs believed to be produced according to desirable practices or to be source verified.

Stable isotope analysis, among other analytical techniques, may be useful for authenticating foods and for detecting

instances of economic adulteration. This is because the stable isotope composition of food items is an inherent feature of the foodstuffs themselves and cannot be lost or easily altered, unlike paper documentation. Many current food tracking techniques rely on marking and monitoring the food packages, rather than the food items contained within, but stable isotope analysis can be directly applied to foods. The information provided by the measured stable isotope ratios varies depending upon the element of interest; thus the analysis of multiple elements within the same sample can be used to investigate several different aspects of the scrutinized food item.

One of the earliest applications of stable isotope analysis to detect economically motivated adulteration was for honey samples imported into the United States. White and colleagues found that the measured $\delta^{13}\text{C}$ values of honey adulterated with the cheaper C_4 -plant sweeteners corn syrup or cane sugar were higher than pure, unadulterated honey (White, 1992; White and Winters, 1989; White et al., 1998). The addition of C_3 -plant sweeteners like beet sugar could be detected by separating and analyzing proteins from the honey and comparing the measured $\delta^{13}\text{C}$ value of the protein to that of the bulk honey; the difference should not be $>1\%$ in unadulterated honeys. These findings led the US Department of Agriculture to adopt carbon isotope measurements as a screening tool to detect adulteration in honey crossing the border (Rossmann, 2001). After implementation, the number of honey samples characterized by suspiciously high $\delta^{13}\text{C}$ values dropped dramatically (White et al., 1998). Carbon stable isotope ratio analysis can also be used to detect the substitution or addition of C_4 sugars to sparkling wines (Martinelli et al., 2003) and beer (Brooks et al., 2002; Rossmann, 2001) as well as the prolific use of corn syrup and cane sugar in purportedly fruit-based jams and jellies (data from J. Ehleringer, published online at <http://4e.plantphys.net/article.php?ch=t&id=391> as a companion to Taiz and Zeiger (2010)).

The stable isotope analysis of oxygen can be used to detect the adulteration of juices labeled as not from concentrate (NFC), an application demonstrated for a variety of fruit juices (Calderone and Guillou, 2008; Houerou et al., 1999; Koziet et al., 1995; Magdas and Puscas, 2011). Recently we analyzed a set of four orange juices, provided to us as blind samples labeled 1–4 and ranging from 0 to 100% NFC juice. The measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the juice waters are presented in Table 2 and Figure 7. If we assume that juice 1 represents 100% NFC juice, and that juice 4 represents 0% NFC juice, then juices 2 and 3 contain between 0% and 100% NFC juice. Using the measured $\delta^{18}\text{O}$ values for 1 and 4, we constructed a mixing model to calculate the proportion (f) of NFC juice in juices 2 or 3: $\delta^{18}\text{O}_{\text{J2or3}} = \delta^{18}\text{O}_{\text{J1}}(f) + \delta^{18}\text{O}_{\text{J4}}(1-f)$. We calculated that juice 2 contained 87% NFC juice while juice 3 contained only 48% NFC juice, very near the true percentages later revealed to be 90 and 50%, respectively. This dataset demonstrates once again the utility of stable isotope analysis for adulteration detection, in this case in the form of juice dilution. The recent introduction of analytical instrumentation that can rapidly measure water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in a variety of liquids of complex matrices without the need for prior water extraction only increases the possible forensic applications for this detection technique (Chesson et al., 2010a; O'Grady et al., 2010a).

Table 2 Measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of four orange juices, provided as blind samples and ranging from 0 to 100% not-from-concentrate juice

Orange juice	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)
1	14.6	3.20
2	10.4	2.55
3	4.5	0.65
4	−4.1	−1.72

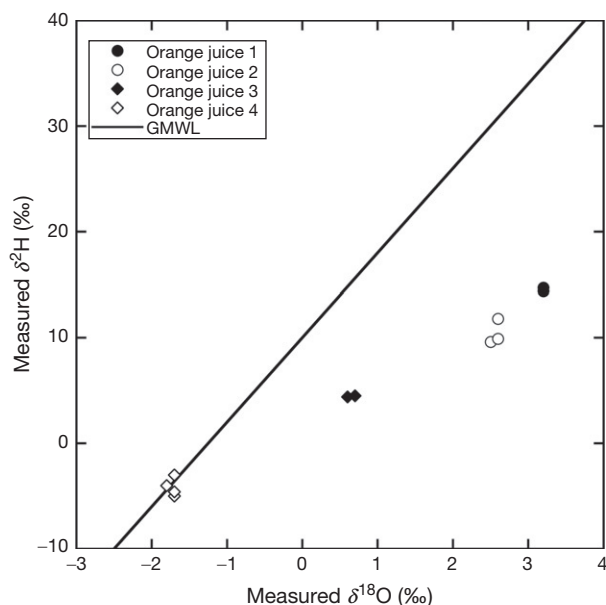


Figure 7 Measured hydrogen and oxygen isotope ratios of four orange juices. Juices were provided as blind samples and ranged from 0 to 100% not-from-concentrate juice. The GMWL ($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10\text{‰}$; Craig, 1961) is shown for comparison.

The stable isotope analysis of carbon, as well as nitrogen, has been used to investigate food production practices for several different food items. Measured $\delta^{13}\text{C}$ values of beef can discriminate between cattle raised organically or on pasture and those raised using a conventional concentrated animal feeding operation (Bahar et al., 2008; Boner and Förstel, 2004; Schmidt et al., 2005a), because most organic and grass-based feeds contain primarily C_3 plants while cattle on feedlots typically consume predominantly C_4 plants. Measured $\delta^{13}\text{C}$ values can be used to discriminate organic and conventional milks (Molkentin and Giesemann, 2010) and to investigate dietary inputs to poultry labeled as corn-fed and sold for premium prices in the European Union (Rhodes et al., 2010). The nitrogen isotope ratios of chicken eggs sold as cage free or free range are typically higher than eggs from battery-raised chickens due to the increased inclusion of animal proteins in foraging chickens (Rogers, 2009), suggesting $\delta^{15}\text{N}$ values could be useful to verify egg labels. Measured $\delta^{15}\text{N}$ values have also been used to differentiate organically versus conventionally grown produce (Bateman et al., 2007; Rogers, 2008; Schmidt et al., 2005b; Stürm and Lojen, 2011), which is possible because the $\delta^{15}\text{N}$

values of synthetic fertilizers typically used in most conventional produce growing regimes are lower than organic fertilizers (Bateman and Kelly, 2007; Vitòria et al., 2004).

Stable isotope ratios, along with trace element abundances, can be used to characterize foods of protected origin (Gonzalvez et al., 2009; Kelly et al., 2005). This application does not rely on mechanistic models to interpret the measured δ -values of various food items with regard to features of production or origin, but instead requires databases of authentic samples to allow for sample-to-sample comparisons (see Figure 1). Nevertheless, this fingerprinting approach can be a powerful tool for investigating economic adulteration in the form of origin or appellation mislabeling. As an example, the European Union maintains a large databank of stable isotope values for wines from the region in order to detect adulteration by comparing samples of suspect appellation to authentic wines (Rossmann, 2001). A combination of light stable isotope analysis and trace element analysis has been used to characterize a variety of other economically important foodstuffs, including butter (Manca et al., 2006), cheese (Pillonel et al., 2003), milk (Sacco et al., 2009), olive oil (Camin et al., 2010a,b), and tomatoes (Bontempo et al., 2011). There is also some evidence that a combination of stable isotope and mineral analysis could be useful for distinguishing organically versus conventionally grown fruits (Camin et al., 2011). For a complete review of the combination of isotope and trace element techniques for discriminating foods, see (Gonzalvez et al. (2009), Kelly et al. (2005), and Rossmann (2001).

14.19.4.2 Food Origin Authentication

Origin authentication of food products is a critical component of consumer protection and represents an ongoing challenge for producers, governmental organizations, and researchers. Recent and much publicized federal recalls within the United States of melons contaminated with *Listeria* (2011) and eggs (2010), peanuts (2009), and tomatoes (2008) contaminated with *Salmonella*, as well as the recall of *E. coli*-tainted spinach (2006), have highlighted the need to rapidly trace the origin of food products. In response to these issues, the US Congress passed the Federal Drug Administration Food Safety Modernization Act (Public Law 111–353) on 21 December 2010 (signed into law on 4 January 2011) that shifts the focus of federal regulators from responding to food contamination to preventing it. Yet many prevention measures proposed and currently in place rely on producer self-regulation and tracking techniques that are dependent on the food containers, rather than the food products themselves.

Stable isotope signatures of food products relate to the region where the product was grown (Oulhote et al., 2011). Specifically, the stable hydrogen and oxygen isotope analysis of food and other organic materials has been shown to relate to environmental water hydrogen and oxygen isotope signatures (see Section 14.19.3.1), and thus geographic or isoscape models could be used for authenticating a food's region of origin. While the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of many plant-based food products have been shown to relate to region of origin, including rice (Suzuki et al., 2008), olive oil (Camin et al., 2010b), coffee beans, (Rodrigues et al., 2009, 2010, 2011), and

juices (Rummel et al., 2010), only US Pacific coast wine $\delta^{18}\text{O}$ values have been modeled within a true geographic context (West et al., 2007). In their study, West et al. (2007) found Washington and Oregon wine $\delta^{18}\text{O}$ values were distinguishable from California wine $\delta^{18}\text{O}$ values. The measured wine $\delta^{18}\text{O}$ values were then used in conjunction with estimated mean annual precipitation $\delta^{18}\text{O}$ values and seasonal climate parameters to develop an isoscape for wine $\delta^{18}\text{O}$ values. Using their model, the authors were successful in predicting wine $\delta^{18}\text{O}$ values for past vintages that were grown under normal climatic condition (non-El Niño/Southern Oscillation years; West et al., 2007). Similar applications have been applied to nonfood plant products including castor beans (West et al., 2010b) and marijuana (Hurley et al., 2010b).

While some food products are associated with discrete geographic regions of production, other foods are produced globally. In these instances, stable isotope analysis may be very powerful compared to other fingerprinting techniques (Gonzalvez et al., 2009; Kelly et al., 2005), as stable isotope models do not require extensive databases of verified products from specific regions to compare isotopic signatures to an unknown sample. An example of such a product is honey and associated honeybee products (i.e., beeswax) given the global distribution of the European honeybee, *Apis mellifera* L., which produces the vast majority of commercially available honey from plant nectar. It has been shown that the hydrogen and oxygen stable isotope analysis of honeycomb wax and protein is useful for geographic origin assignment (Chesson et al., 2011b; Schellenberg et al., 2010; Tipple et al., 2012). Chesson et al. (2011b) found beeswax $\delta^2\text{H}$ values were correlated with both mean annual precipitation $\delta^2\text{H}$ values and locally available tap water $\delta^2\text{H}$ values for a given hive location. In an associated study, Tipple et al. (2012) noted similar relationships between beeswax compound-specific $\delta^2\text{H}$ values and both mean annual precipitation $\delta^2\text{H}$ values and tap water $\delta^2\text{H}$ values. The geochemistry of residues like beeswax is discussed in more detail in Chapter 14.20.

Here, we combine published datasets of beeswax and compound-specific $\delta^2\text{H}$ values with data from an additional 33 US verified locations. All samples were analyzed following methods outlined in Chesson et al. (2011b) and Tipple et al. (2012). We found similar relationships to those initially published between measured beeswax $\delta^2\text{H}$ values and estimated mean annual precipitation $\delta^2\text{H}$ values where $\delta^2\text{H}_{\text{bulk}} = 0.7 \times \delta^2\text{H}_{\text{ppt}} - 218\text{‰}$ ($F_{1,62} = 131.1$, $p < 0.0001$, $r^2 = 0.68$) and $\delta^2\text{H}_{\text{alkane}} = 0.9 \times \delta^2\text{H}_{\text{ppt}} - 197\text{‰}$ ($F_{1,62} = 138.1$, $p < 0.0001$, $r^2 = 0.69$) (Figure 8). A subset of beeswax bulk and *n*-alkane fractions were measured and used to estimate the $\delta^2\text{H}$ value of mean annual precipitation for three hives of known location. We found the bulk beeswax/*n*-alkane fraction from hives located in McVile, North Dakota; Nelson, Nebraska; and Anderson, South Carolina had $\delta^2\text{H}$ values of $-288/-283\text{‰}$, $-274/-251\text{‰}$, and $-242/-230\text{‰}$, respectively. Using the relationships between compound-specific beeswax $\delta^2\text{H}$ values and precipitation, we estimated precipitation $\delta^2\text{H}$ values of -99 , -62 , and -38‰ for McVile, Nelson, and Anderson, respectively. The calculated mean annual precipitation $\delta^2\text{H}$ values $\pm 13\text{‰}$ (root mean square error of the regression) was then used to predict the potential geographic regions of origin of the three beeswax samples. Predicted regions and verified

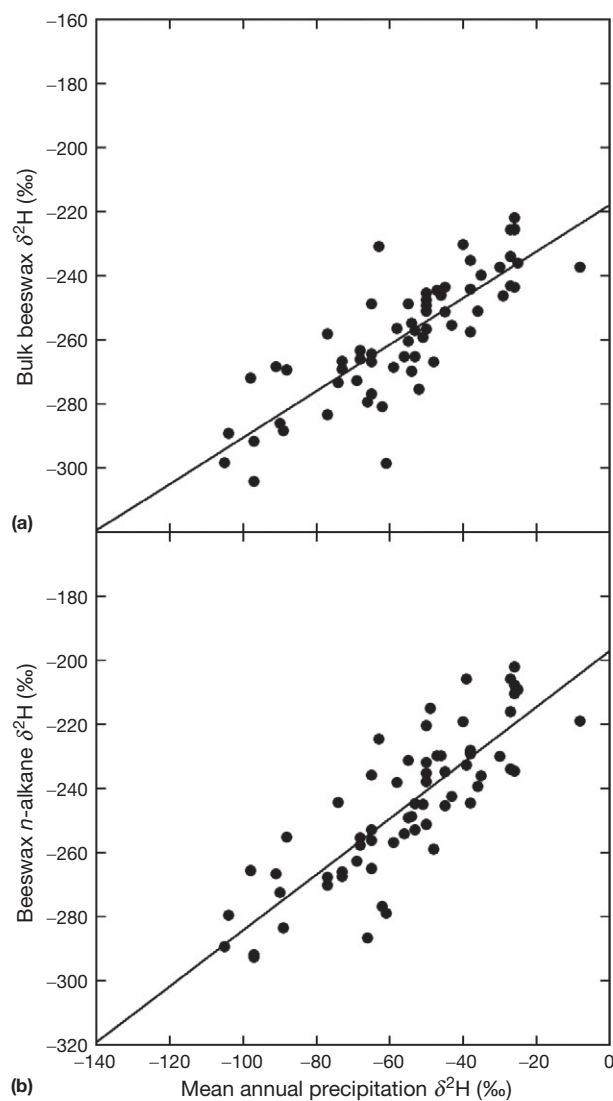


Figure 8 Hydrogen isotope ratios measured for bulk beeswax (a) and *n*-alkanes extracted from beeswax (b) compared to mean annual precipitation (ppt) estimated for collection locations. The data were positively and significantly correlated. Regression lines are described by the equations $\delta^2\text{H}_{\text{bulk}} = 0.7 \times \delta^2\text{H}_{\text{ppt}} - 218\text{‰}$ ($F_{1,62} = 131.1$, $p < 0.0001$, $r^2 = 0.68$) for panel (a) and $\delta^2\text{H}_{\text{alkane}} = 0.9 \times \delta^2\text{H}_{\text{ppt}} - 197\text{‰}$ ($F_{1,62} = 138.1$, $p < 0.0001$, $r^2 = 0.69$) for panel (b).

locations for the three hives are shown in Figure 9, generated using a mean annual precipitation hydrogen isoscape as input (see Section 14.19.3.1). This simple exercise illustrates the potential usefulness of stable isotope analysis and geospatial modeling for forensic and geolocation applications. It also highlights how the technique does not produce predictions specific to one particular region, but rather predicts zones of likelihood.

14.19.4.3 Controlled Substances Produced from Plants

14.19.4.3.1 Cocaine and heroin

Seizures of illicit plant-derived drugs, like cocaine and heroin, are unfortunately a common occurrence and there exists

an intense interest in developing analytical methods for identifying the origin of these narcotics. Many of the available techniques for analyzing drugs are focused on elemental or chromatographic characterization and, as such, have limited potential in revealing information on possible origins (Besacier et al., 1997; López-Artíguez et al., 1995; Sperling, 1991). Both cocaine and heroin are derived in whole or in part from natural sources, and thus the stable isotopic compositions of these drugs should record something of the growth conditions experienced by the parent plant materials, coca leaves (*Erythroxylon coca*), and opium poppy (*Papaver somniferum*), respectively. There exist a few principal areas of drug production, namely regions of Bolivia, Peru, and Columbia for cocaine (Ehleringer et al., 2000); and Southwest Asia, Southeast Asia, Mexico, and South America for heroin (Ehleringer et al., 1999). The limited potential regions of origin for these narcotics could be extremely useful in the application of stable isotope analysis due to the large environmental variability characterizing the regions.

A 1999 study by Ehleringer and colleagues found that a combination of measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values could discriminate heroin from four major growing regions, with very little overlap between the isotopic compositions of individual samples known to originate in Southwest Asia, Southeast Asia, Mexico, and South America. The derivatization of heroin to morphine increased the discriminatory power of ^{13}C and ^{15}N by minimizing isotopic variation within sample groups (Ehleringer et al., 1999). The authors also found evidence that measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values could be used to discriminate between potential source regions for a smaller dataset of authentic, known-origin cocaine specimens analyzed as blind samples. This preliminary result was later corroborated using a much larger dataset of cocaine samples ($n=200$) from three South American countries. With a combination of only C and N isotope compositions of cocaine, 90% of samples were correctly assigned a country of origin. Additional measurements of the amounts of two trace alkaloids extracted from the cocaine specimens increased assignment accuracy to 96% (Ehleringer et al., 2000).

Recently, a real-world example of the application – and existing limitations – of stable isotope analysis for determining the origin of seized plant-based drugs was described. In April 2003, six packages were transferred from the merchant vessel *Pong Su* to Australia as the North Korean-flagged ship passed close to the country's coast. Two of these packages were confiscated days later from the trunk of a car and three more were found buried in the town of Lorne. To date, the sixth package has not been recovered. Found inside each of the five seized packages were 72, ~350 g blocks of heroin, a total recovered weight of >125 kg. Core samples from 100 of the heroin blocks were chemically profiled (Collins et al., 2006) and measured for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values (Casale et al., 2006). Results of the stable isotope analyses demonstrated that the combination of carbon and nitrogen isotopic compositions for the *Pong Su* heroin samples was unlike any authentic samples previously measured from Southwest Asia, Southeast Asia, Mexico, or South America, suggesting a yet-to-be-determined fifth potential source for heroin (Casale et al., 2006) and illustrating the need for additional collections of seizures from more regions of origin.

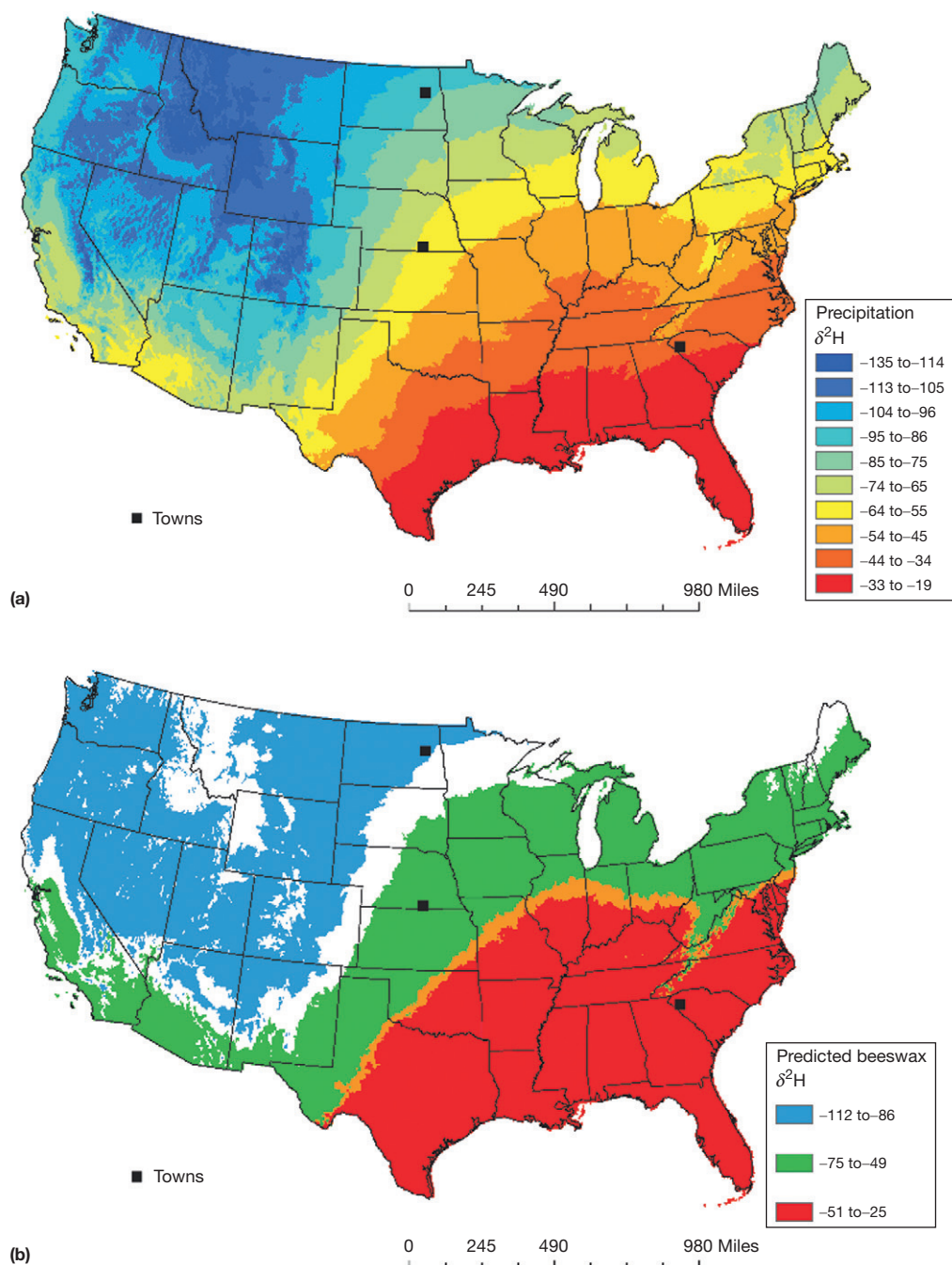


Figure 9 The predicted geographic distribution of hydrogen isotope ratios in precipitation across the United States (a) and regions of precipitation consistent with the measured $\delta^2\text{H}$ values of three beeswax *n*-alkane samples (b). Towns where samples originated are shown with black squares. See text for a complete description of prediction region generation.

14.19.4.3.2 Marijuana

Marijuana is a narcotic of natural source, derived from the plant *Cannabis sativa* L. Thus, stable isotope analysis has potential utility in understanding both the environmental conditions experienced by and the potential source of cultivated *Cannabis*. Marijuana is the most widely available illicit drug in the world and its use poses a particularly significant public safety threat in the United States (Beaubien, 2010; Rosner, 2007). There are multiple potential sources of the contraband

marijuana that is available in the United States, including *Cannabis* plants cultivated locally or regionally to the point of seizure as well as plants sourced across the border, trafficked from either Canada or Mexico. In order to aid in the development of new enforcement policies and to help eradication efforts focused on the production and sale of marijuana, it would be extremely beneficial to supply drug enforcement agencies with as much information as possible on the potential origin of drug seizures.

Studies of Brazilian marijuana seized from three distinct regions in the country revealed that the measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of *Cannabis* were useful indicators of the environment under which the plants were grown and could provide details about cultivation conditions (Shibuya et al., 2006, 2007). For instance, marijuana plants with $\delta^{15}\text{N}$ values near 0‰ were often grown near legumes, which fixed atmospheric N_2 with a $\delta^{15}\text{N}$ value of 0‰. Relatively high (approximately +24‰) $\delta^{13}\text{C}$ values were observed in plants grown in dry regions because the increased water stress on these C_3 plants caused a decline in stomatal response and reduced the fractionation of ^{13}C from the atmosphere into plant tissues (Shibuya et al., 2006). For marijuana cultivated indoors rather than outdoors, $\delta^{13}\text{C}$ values are typically low (often $< -30\text{‰}$) if the grower supplied bottled CO_2 from a fossil fuel source to the growing plants. Studies of US marijuana seizures (Booth et al., 2010; West et al., 2009b) have capitalized on the observed differences in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values related to cultivation practices and defined thresholds for determining whether a seized specimen was indoor grown, indoor or shade grown, or outdoor grown using carbon isotopic compositions and whether a plant had inorganic (or no) fertilizer or organic fertilizer applied using nitrogen isotope compositions. Although measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are useful for investigating the growing methods of US marijuana, they do not provide any geographic source information per se (West et al., 2009b).

The use of additional elements – such as hydrogen, oxygen, and even strontium – may be more useful for investigating region of origin for *Cannabis* seizures within the United States (Booth et al., 2010; Hurley et al., 2010ab; West et al., 2009a,b). Recently, Hurley et al. (2010a) described a model for predicting the regional origin of seized marijuana samples using the measured $\delta^2\text{H}$ value for the specimen and an assessment of the location of seizure; possible region predictions included Mexico, eastern United States, western United States, eastern Canada, and western Canada. The authors found that using only the two parameters the model correctly assigned region of origin to 67% of 60 marijuana samples provided in a blind test. Prediction accuracy was increased to 73% with the additional information that all samples were known to have been grown in the United States, removing the across border origins from consideration (Hurley et al., 2010a). While not perfect, this model approach displayed significant promise in the investigation of potential origin for seizures from different metropolitan areas and could potentially supply independent corroboration of drug trafficking trends in the United States currently estimated by drug enforcement agencies (Hurley et al., 2010b).

14.19.4.4 Wood and other Plant Product Isotope Records

Plant products are used in an untold number of commercial goods ranging from clothing to currency to next-generation 'green' products such as glues and biofuels. The diversity of plant products used in commercial goods includes both individual compounds (i.e., cellulose, waxes, phytochemicals) and bulk plant materials (i.e., wood). This diversity requires isotope chemists to use a wide variety of analytical instrumentation and techniques to understand and answer questions

regarding isotope signals in plant materials. Much of the basic research using isotope analysis of plant products has focused on questions of plant physiology, ecosystem dynamics, and geologic applications, but hydrogen, carbon, and oxygen stable isotope analyses of plant products have also been shown useful in answering many questions of forensic interest.

14.19.4.4.1 Arson – isotopic comparisons

Wooden matchsticks are commonly associated with many arson crime scenes and investigations. Most wooden matchsticks in Europe and North America derive from the wood of the aspen tree (*Populus* sp.; Farmer et al., 2005) and stable isotope analysis has been used to discriminate unburned matchstick batches and manufacturers based on unique bulk $\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values (Farmer et al., 2005, 2007). In real-world forensics cases it is more likely to find burned matchsticks at the scene of a fire. Stable isotope analysis of bulk burned and unburned matchsticks originating from the same batch showed no statistically significant difference, suggesting stable isotope ratio measurements have utility for unknown-known comparisons even if burned matchsticks are recovered (Farmer et al., 2009a). In addition, Farmer et al. (2009a) found that gasoline-assisted fire ignition and fire extinguisher usage had no significant effect on the stable isotope values of the collected matchstick specimens.

14.19.4.4.2 Flavor compounds – adulteration detection

Vanilla is one of the most widely used flavors in the food industry and it is also important to the pharmaceutical and fragrance industries. Natural vanilla is prized for its complex flavor profile and demands a premium price, while synthetic vanilla can be cheaply and easily produced. Natural vanilla is extracted from the pods of tropical orchids while synthetic vanilla is manufactured from lignin and other chemical feedstock. Detecting synthetic vanilla using stable isotope analysis has been an area of active research for over 40 years; initial findings showed that natural vanillin from orchids was more enriched in ^{13}C than synthetic vanillin from wood pulp (Bricout et al., 1974). These results are consistent with vanilla orchids utilizing the crassulacean acid metabolism photosynthetic pathway and trees using the C_3 photosynthetic pathway (Farquhar et al., 1989). This difference became the basis for a test of vanilla authenticity (Hoffman and Salb, 1979) similar to the honey authenticity test (White and Winters, 1989; White et al., 1998). Vanilla manufacturers circumvented these authenticity tests by mixing ^{13}C -enriched vanillin with lignin-derived vanillin, a practice which in turn led to the successful development of several authentication methods that used the stable carbon isotope ratios of individual methyl and carbonyl groups to distinguish between natural and synthetic vanillin (Krueger and Krueger, 1983, 1985). Most recently, Greule et al. (2010) showed natural and synthetic vanillins have a distinct combination of $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values for both bulk vanillin and specific methoxyl groups.

14.19.4.4.3 Plant and wood products – geographical region of origin

Stable isotope analysis has been found relevant to determine the geographical origin of wood and other plant products. Hydrogen, carbon, and oxygen isotopic analyses of wood

have traditionally been focused on tree-ring analysis (Dawson et al., 2002), with the goal of understanding past climates (Jahren and Sternberg, 2008). Initial work on tree rings used bulk wood, but individual organic components (i.e., lignin, cellulose, and hemicellulose) have been shown to differ isotopically (Epstein et al., 1976; Wilson and Grinstead, 1977). With this in mind, the nonexchangeable H fraction of cellulose is used most commonly for $\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ analysis (Roden and Ehleringer, 1999), but other components can also be used for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements.

The geographical origin of trees and wood products is needed to limit illegal trade of forest products, which has been linked to the introduction of insect pests and deforestation through illegal logging practices. Stable isotope analysis has proven useful to ensure traceability of wood products as the isotope ratios of wood products relate to the region where the product was grown (Oulhote et al., 2011). Specifically, the stable hydrogen and oxygen isotope analyses of wood and other plant materials have been shown to relate to environmental water hydrogen and oxygen isotope signatures (see review by Bowen, 2010a and Section 14.19.3.1). Given the relationship between the stable hydrogen and oxygen isotope ratios of organic materials and environmental waters, geographic or isoscape models can be used for authenticating a product's region of origin. As an example, Keppler et al. (2007) investigated the $\delta^2\text{H}$ values of lignin methoxyl groups extracted from wood that were derived from a global dataset and found statistically significant correlations to environmental water $\delta^2\text{H}$ values. The authors found much weaker correlations between bulk wood and environmental water $\delta^2\text{H}$ values, likely due to exchangeable H atoms within bulk wood (Keppler et al., 2007). To assess potential differences in the isotopic signatures of Asian and European commercial wood, bulk $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements of Siberian and Austrian larch wood demonstrated the utility of using two elements together to identify potential regions of origin (Horacek et al., 2009). In this example, Horacek et al. (2009) found larch woods from the different continents had overlapping $\delta^{13}\text{C}$ values, but nonoverlapping $\delta^{18}\text{O}$ values. Carbon isotope ratios have also been used in combination with tree-ring width patterns to assess region of origin of wood in the southwestern United States with some success, but this technique requires extensive databases of known tree-ring width patterns for specific regions (Kagawa and Leavitt, 2010).

In spite of the promising results summarized above, no study of a forest product has attempted to link observations with modeled $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values within a true geographic context. On the other hand, cotton cellulose and castor bean oil $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values have been modeled and predictive isoscape projections have been produced (West et al., 2010b). These models potentially could be used to infer the source of counterfeit currency and ricin poison, respectively.

14.19.5 Human-Related Forensic Applications of Stable Isotope Analysis

14.19.5.1 Dietary Patterns

The stable isotope ratio analysis of the elements carbon, nitrogen, and sulfur can provide information on food items

consumed by both modern and ancient man because the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ values of human tissues record aspects of nutrition and food choice. Plants in warmer, drier climates typically use the C_4 pathway and are characterized by $\delta^{13}\text{C}$ values of -14 to -10‰ while plants in cooler, wetter climates generally use the C_3 photosynthetic pathway and have measured $\delta^{13}\text{C}$ values of -30 to -20‰ (Cerling et al., 1997). Animals incorporate the carbon isotope ratio of plants within the diet into tissues with some slight fractionation between diet and tissue (Peterson and Fry, 1987), and thus ^{13}C can be used to trace the flow of organic matter from plants to animals within a food web. The $\delta^{15}\text{N}$ values of individuals within a food web can also be used to track the flow of organic matter. There is a larger diet–tissue fractionation for nitrogen isotopes than for carbon isotopes, whereby ^{15}N is typically enriched in a stepwise fashion approximately 2–3‰ for each trophic level (Post, 2002; Robbins et al., 2005). Sulfur is a conservative recorder, with little to no fractionation between dietary food items and animal tissues, and sulfur stable isotope ratios can be used to investigate coastal versus inland diets because the $\delta^{34}\text{S}$ values of marine proteins are relatively higher than those of land animals (Peterson and Fry, 1987).

Citizens of different geographic regions often consume different types of foods due to cultural dietary traditions and preferences, which could impact the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ values of bulk diet. The consumption of meat and other animal products (e.g., eggs and milk) varies globally (Speedy, 2003) and can significantly impact the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of human hair, as demonstrated in studies of modern omnivores, vegetarians, and vegans (O'Connell and Hedges, 1999; Petzke et al., 2005a,b). Agricultural practices can also impact the isotopic composition of available food items. In the United States, where the C_4 plants like corn (maize) and sugar cane are found in many human – and livestock – foodstuffs, the $\delta^{13}\text{C}$ value of hair is typically higher than that of humans consuming more C_3 plants, such as residents of European countries (McCullagh et al., 2005); see Figures 6 and 7 in Chapter 14.23 (and also Figure 13 of Bowen (2010a)). There have been several studies published recently that document dietary-driven differences in modern human tissue $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ values including hair collected in Asia (Thompson et al., 2010), hair and fingernails from North and South Americans (Nardoto et al., 2006), and hair procured globally (Mützel (Rauch) et al., 2009).

The differences in diet – and thus body tissue – carbon, nitrogen, and sulfur isotopic composition related to consumption patterns are useful when distinguishing natives from travelers or recent immigrants in both modern (Fraser et al., 2006; Mützel (Rauch) et al., 2009) and historic (Schwarcz et al., 2010) forensic investigations. Bol et al. (2007) found a combination of measured $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ values (as well as $\delta^{18}\text{O}$ values) could be used in a principal component analysis to distinguish European natives from recent non-European arrivals. Carbon, nitrogen, and sulfur stable isotope analyses have also proven useful in the investigation of Incan child mummies, revealing information on the possible diet and socioeconomic status of the victims chosen for sacrifice (Wilson et al., 2007). The application of stable isotope analysis to investigate ancient dietary patterns is fully described in Chapter 14.21.

14.19.5.2 Spatial Patterns

It is well established that the hydrogen and oxygen isotopic composition of human tissues are directly related to the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of drinking water imbibed by the subject, a fact that can be exploited to predict the isotopic composition of water in an inverse fashion from the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of hair or urine (Ehleringer et al., 2008; O'Brien and Wooller, 2007; O'Grady et al., 2010a; Sharp et al., 2003). It is then possible to use these water predictions to infer the possible geographic origin and travel history of a subject of interest because the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of environmentally derived drinking water vary across discrete regions (see Section 14.19.3.1; Bowen and Revenaugh, 2003; Bowen et al., 2007b). Thus, the hydrogen and oxygen stable isotope ratio analysis of human tissues can reveal spatially relevant patterns in human movement and settlement (Bowen et al., 2009; Fraser et al., 2006).

In many cases, researchers have been constrained to using simple linear regression models as proxies for the complex physiological mechanisms regulating the incorporation of water H and O atoms into human tissues. Recently a series of semimechanistic process-based models for describing the relationship between water and tissue $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values has been published. These models have primarily focused on human hair (Bowen et al., 2009; Ehleringer et al., 2008; Thompson et al., 2010) but are currently being expanded to the body water pools of a small rodent (Podlesak et al., 2008) and humans (Ehleringer et al., 2010). For a detailed discussion of the use of hair stable isotope analysis for understanding the movement of animals, see Chapter 14.23. Isotopic differences in tissues driven by human physiology are discussed in Chapter 14.22. Here, we focus on the forensic use of hydrogen and oxygen stable isotope analysis to understand spatial patterns propagated in a variety of human tissues, including body water, tooth and bone minerals, and hair proteins.

14.19.5.2.1 Body water, geography, and metabolism

The hydrogen and oxygen isotopic composition of body water is influenced by the constituent inputs to the pool – drinking water, food, food water, and O_2 – and losses in the form of urine, sweat, and water in exhalations (Kohn, 1996; Luz et al., 1984; Schoeller et al., 1986). In humans, imbibed fluids (most of which are water based) are the largest contributor to the body water pool and the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the body water pool is thus directly linked to geography through the consumption of local water (see also Section 14.19.3.2). It is possible to generate body water isoscapes for humans (Ehleringer et al., 2010), although the relationship between predicted body water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values and local water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values is not 1:1 due to the impact of food and O_2 . The predictability of the hydrogen and oxygen isotopic compositions of human body water described by Ehleringer et al. (2010) has recently been tested using body water (urine) collected from residents of Salt Lake City, Utah, USA, confirming that the measured data generally match predictions modeled from the isotopic composition of drinking water available to the subjects (Figure 10, data courtesy of Shannon O'Grady).

Metabolic water generated as a result of physiology can impact the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the body water pool,

allowing investigations into an individual's activity level or water use (Kohn, 1996; McKechnie et al., 2004). Kreuzer-Martin and colleagues demonstrated that metabolic water had a large impact on the total body water pool of bacteria during log-phase growth (Kreuzer-Martin et al., 2005, 2006), while Podlesak et al. (2008) found the isotopic contribution of food via metabolic water generation to wood rat body water was substantial for both H (29%) and O (15%). Variation in the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of body water collected from individuals living in the same area and drinking the same water (Figure 10), is likely due to variation in metabolically generated water due to physiology and activity level.

Change in the isotopic signal of the body water pool is rapid after a change in drinking water (O'Brien and Wooller, 2007; Podlesak et al., 2008; Sharp et al., 2003) and the body water of a transient will quickly mirror the isotopic composition of local residents. This change will eventually be recorded in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of body proteins (O'Brien and Wooller, 2007; Sharp et al., 2003), allowing for investigations into the drinking water changes of an individual using the sequential hydrogen and oxygen isotope analysis of a continuously growing proteinaceous tissue (Ehleringer et al., 2010; Hobson et al., 2010). Using a semimechanistic protein-isotope model developed for modern human hair collected in the United States (Ehleringer et al., 2008), Ehleringer et al. (2010) demonstrated that it is possible to calculate the isotopic composition of drinking water, and thus geographic location of a human subject, from the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of their hair keratin. The forensic applications of human hair hydrogen and oxygen isotope ratio analysis are explored more fully in Section 14.19.5.2.3 and in Chapter 14.23.

14.19.5.2.2 Carbonates and phosphates in teeth and bones

The $\delta^{18}\text{O}$ value of both carbonates and phosphates within tooth and bone bioapatite records the isotopic composition of an animal's body water pool among other factors (e.g., diet, ambient humidity), and thus is linked to local water composition (see review by Kohn and Cerling, 2002). The oxygen isotope analysis of bioapatite has proven particularly useful for investigating paleoecology and paleoclimate via fossil remains of animals (Koch, 1998). This is because phosphate and, to a lesser degree, carbonate are generally resistant to degradation and the relationships between the measured $\delta^{18}\text{O}$ value of the two components is well established (Bryant et al., 1996; Daux et al., 2008; Iacumin et al., 1996), so either can be considered a reliable measure of environmental water. However, relatively few studies have investigated the link between drinking water, body water, and bioapatite $\delta^{18}\text{O}$ values in modern animals, specifically humans (D'Angela and Longinelli, 1990; Longinelli, 1984).

Recently, Ehleringer et al. (2010) published a model to describe the relationship between drinking water and tooth carbonate $\delta^{18}\text{O}$ values for modern humans. The model was used to produce a spatial representation of the predicted tooth carbonate oxygen isotope ratios of US residents (Ehleringer et al., 2010), which was then applied to samples of teeth collected from unidentified murder victims (Ehleringer et al., 2010; Schwarcz et al., 2010). Because the teeth were formed at 8–13 years of age, the measured $\delta^{18}\text{O}$ values of the tooth carbonate

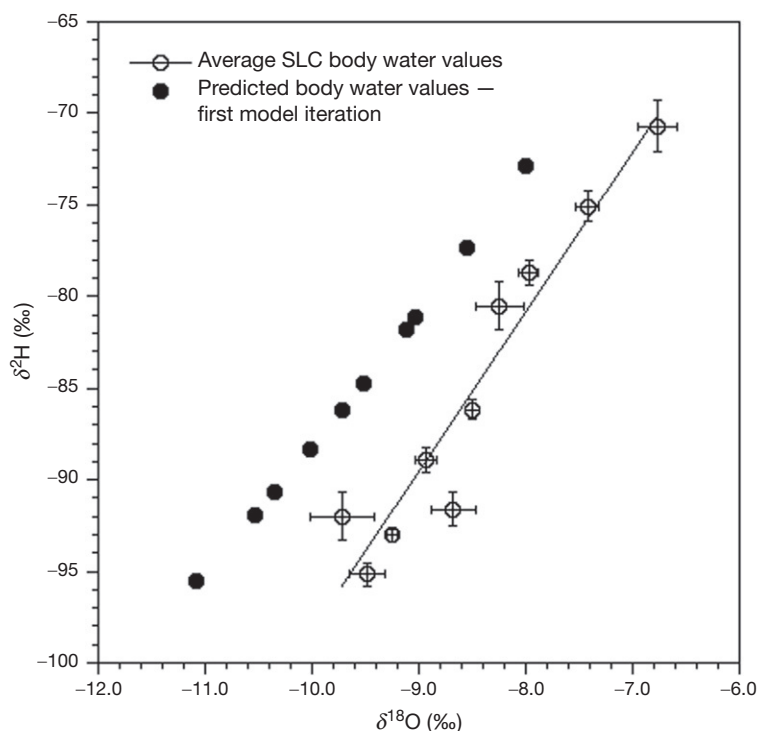


Figure 10 Measured (open circles) and modeled (closed circles) hydrogen and oxygen isotope ratios of body water for modern humans living in the metropolitan area of Salt Lake City, Utah, USA. See Ehleringer et al. (2010) for a description of the body water model. Data courtesy of Shannon O'Grady.

could be used to back-calculate the isotopic composition of drinking water during tooth formation, potentially aiding investigators by identifying if the victim was a local resident (or not) of a region during young adulthood. By comparing predicted origin based on analyzed tooth bioapatite to predicted origin based on the analysis of a tissue that records more recent history (i.e., hair) it may be possible to reconstruct some of the movement or migration history for an individual. A case example of using oxygen isotope analysis of modern human tooth enamel during a forensic investigation is presented in Section 14.19.5.3.

14.19.5.2.3 Proteins in bone and hair

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of proteinaceous tissues record body water isotopic composition and thus, potentially, record location information. The $\delta^2\text{H}$ values of bone (Cormie et al., 1994; Leyden et al., 2006; Reynard and Hedges, 2008) and tooth (Kirsanow et al., 2008) collagen are related to climate (i.e., through local water $\delta^2\text{H}$ values). A relationship between environmental water and body tissue $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values has also been documented for human hair keratin (Ehleringer et al., 2008; O'Brien and Wooller, 2007; Sharp et al., 2003) as well as bird feathers (Hobson et al., 1999; Wolf et al., 2011), bacterial spores (Kreuzer-Martin and Jarman, 2007; Kreuzer-Martin et al., 2003), meat from beef cattle (Bong et al., 2010; Horacek and Min, 2010; Nakashita et al., 2008), freshwater fish muscle tissue (Solomon et al., 2009; Whitedge et al., 2006), and hair from nonhuman primates (Chenery et al., 2011). The history recorded by hair proteins is, in many cases, much shorter

than that of proteins in bone or teeth, which could allow investigators to reconstruct multiple periods of history for an individual.

The analysis and interpretation of the hydrogen isotope ratios of proteinaceous tissues, in particular, requires some caution due to the presence of exchangeable H atoms within the protein structures. This exchangeable hydrogen fraction will reflect the isotopic composition of water vapor in the ambient laboratory atmosphere and can impact the total measured $\delta^2\text{H}$ of a sample. Several methods have been published describing the calculation and control of the exchangeable H fraction in bone (Cormie et al., 1994; Sauer et al., 2009), hair (Bowen et al., 2005a; Chesson et al., 2009), and other keratinous materials (Wassenaar and Hobson, 2000, 2003) during hydrogen isotope analysis.

Based on previously published models describing the relationship between human hair keratin $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (Bowen et al., 2009; Ehleringer et al., 2008), it has been recently hypothesized that the proteinaceous tissues of all animals should display a linear relationship between measured hydrogen and oxygen isotope ratios (Wolf et al., 2011). We tested this hypothesis using data for hair collected from domesticated animals – including cats, cows, dogs, goats, horses, rabbits, sheep, and yaks – and found a strong linear relationship between measured hair (nonexchangeable) hydrogen and oxygen isotope ratios (Figure 11). Interestingly, the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of hair from cats and dogs grouped together in isotope 'space,' above the ordinary least squares regression line describing the relationship for all other animals ($\delta^2\text{H} = 6.4 \times \delta^{18}\text{O} - 206\text{‰}$, $r^2 = 0.92$). The regression for all

other animals was very similar to the relationship between modern human hair keratin $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values ($\delta^2\text{H} = 5.7 \times \delta^{18}\text{O} - 166\text{‰}$, $r^2 = 0.87$; Ehleringer et al., 2008).

The difference between the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of hair from domesticated cats and dogs and all other animals in the dataset (Figure 11) could be due to the differences in physiology for pets living a (relatively) relaxed lifestyle versus those animals that are often more active. The difference could be due to dietary characteristics, as cats and dogs are carnivorous by nature while the other animals are herbivorous browsers and grazers. In addition, we would assume cats and dogs kept as pets often consume the same purchased food day to day (e.g., a supermarket diet) while the diet of goats, horses, and sheep living out of doors will include more local foods.

14.19.5.3 Provenancing Unidentified Homicide Victims

A natural extension of measuring hair $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values is geolocation during the investigation of homicide victims with no known identity or history. Much of the proof-of-concept research to establish this use of stable isotope analysis is presented in Chapter 14.23. The hydrogen and oxygen stable isotope analysis of unidentified human remains can be useful in cases where traditional investigative methods, such as screening missing person reports or conducting DNA analysis, have proven inconclusive. In these instances, the goal of isotope analysis is to aid investigators in narrowing potential regions of origin for the victim by answering questions related to travel history: Did the victim move prior to death? Was the individual a resident of the region in the months before death?

Stable isotope analysis of human hair remains was applied recently in the case of an unidentified murder victim found in September 1971 in Stanislaus County, California, USA known only as 'Jane Doe.' The case was reopened in 2008 and several strands of hair from the victim were submitted for stable isotope analysis to elucidate the travel history of the young lady prior to her death. The hair sample was sectioned into lengths approximately equivalent to 1 week intervals. The measured $\delta^{18}\text{O}$ values of the hair sample showed little weekly variation in the 9 month period before death (Figure 12). This suggests there was little to no change in the isotopic composition of her drinking water and therefore little to no movement or travel by the victim. Using the published hair–drinking water isotope model (Ehleringer et al., 2008) in an inverse fashion and an average $\delta^{18}\text{O}$ value of 10.9‰ for the analyzed hair, the modeled drinking water $\delta^{18}\text{O}$ value for the victim was $-12.0 \pm 0.5\text{‰}$. Regions in the continental United States characterized by this drinking water value are shown in Figure 13 (a) and (b). The ^{18}O content of enamel carbonate from a tooth was also analyzed and used to model the isotopic composition of childhood drinking water and thus childhood origin (see Section 14.19.5.2.2; Figure 13(c)). As seen in Figure 13, predicted regions were very similar for both the measured hair and tooth $\delta^{18}\text{O}$ values.

Jane Doe is now positively identified as Mary Alice Willey and much is known about her short life, which is consistent with the observed isotope data. Mary Alice was born and raised in Anaheim, California and moved to San Francisco, California in September 1970 to attend college, a year before her death and her body's discovery in Stanislaus County in 1971. Shortly after enrolling in classes, she grew disillusioned with school

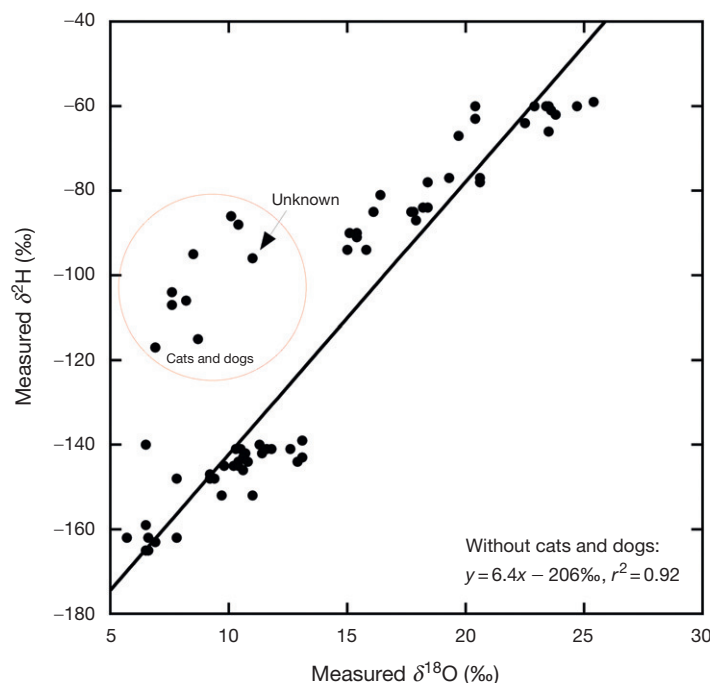


Figure 11 Measured nonexchangeable hydrogen and total oxygen isotope ratios of hair collected from a variety of domesticated animals. Shown is the regression line for animals excluding cats and dogs. The line is described by the equation $\delta^2\text{H} = 6.4 \times \delta^{18}\text{O} - 206\text{‰}$, $r^2 = 0.92$.

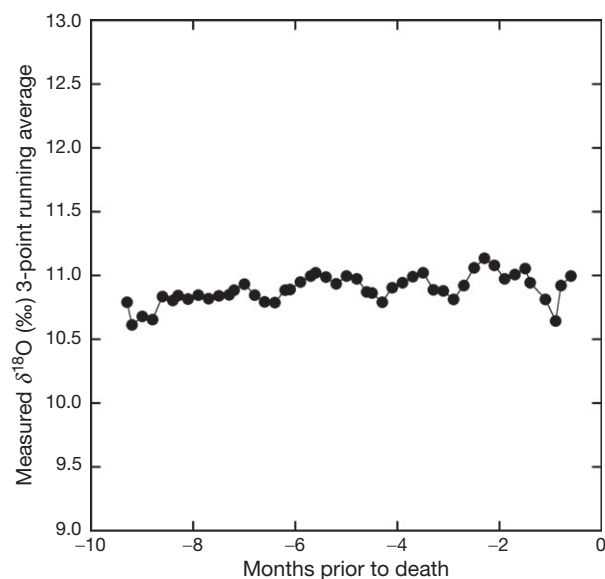


Figure 12 Measured oxygen isotope ratios of human hair remains from an unidentified murder victim found in Stanislaus County, California, USA in 1971. Time was calculated using an average hair growth rate of 0.4 mm day^{-1} . Presented data are 3-point running averages.

and became involved in the Black Power movement. Records suggest she may have participated in the smuggling of a gun to George Jackson, a San Quentin prisoner, which resulted in the killings of several prison guards and the death of Jackson during an escape attempt. Seven days after the incident, a woman fitting the description of Mary Alice entered a San Francisco police station to report a missing purse. After completing paperwork, she signaled to individuals outside the station, who entered and killed policemen in apparent retaliation for George Jackson's death. Thirteen days later the body of Mary Alice Willey was discovered floating in a canal ditch in Stanislaus County.

14.19.5.4 Human Diseases

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of body water are impacted by physiology and might therefore be used to detect nonsteady states (e.g., disease states). The combined influxes and effluxes from the body water pool are described as the total water flux (TWF) for an individual. For humans, approximate percentages of the major inputs – drinking water (43%), food water (30%), and atmospheric O_2 (20%) – as well as sweat and urine outputs (63%) for the body water pool are known (O'Grady et al., 2010b). Increased TWF in the form of increased drinking water consumption has been hypothesized to impact the isotopic composition of the body water pool, causing the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of body water to approach that of drinking water (Chesson et al., 2010b; Clementz et al., 2008). O'Grady et al. (2010b) have shown that the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of body water are indicators of diabetes mellitus in mice; the isotopic composition of body water in diabetic mice with increased TWF more closely resembled the isotopic composition of supplied drinking water than the body water of healthy mice. The isotopic composition of body water might therefore be useful for

diagnosing disease states that affect drinking water consumption, providing a rapid, inexpensive screening technique.

Measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of human hair samples can also be useful for detecting disease states. For example, there are systematic, predictable changes in the carbon and nitrogen isotopic composition of hair collected from individuals suffering from eating disorders (Hatch et al., 2006; Mekota et al., 2006). Mekota et al. (2006) found that a recovering patient's body mass index was inversely correlated with the measured $\delta^{15}\text{N}$ value of newly produced hair as body tissue catabolism decreased with the increase in food intake and body weight. Hatch et al. (2006) developed a stepwise discriminate analysis function to classify subjects as recovering anorexics, recovering bulimics, or healthy individuals using both measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of collected hair. Petzke et al. (2006) studied patients with cirrhosis of the liver, a disease that affects the metabolism of proteins and amino acids, and found that the bulk measured $\delta^{15}\text{N}$ values of hair from liver cirrhotic patients were lower than the bulk $\delta^{15}\text{N}$ values of hair collected from healthy individuals. This difference was attributed to differences in the $\delta^{15}\text{N}$ values of individual amino acids incorporated during hair synthesis (Petzke et al., 2006).

There is potential to use the measured carbon and nitrogen stable isotope ratios of various human tissues as nutritional biomarkers (Jahren et al., 2006; Kraft et al., 2008; Nash et al., 2009; O'Brien et al., 2009; Yeung et al., 2010). Jahren et al. (2006) suggested that the $\delta^{13}\text{C}$ values of foods and beverages commonly consumed in the modern American diet could be used to estimate the proportion of high fructose corn syrup and/or cane sugar sweeteners contained within the different food items. Yeung et al. (2010) extended this work by measuring the $\delta^{13}\text{C}$ values of human blood serum collected from individuals consuming either low or high quantities of corn- or cane-sweetened beverages and found that the carbon isotope ratios of serum were higher in individuals drinking more sweetened beverages. The $\delta^{15}\text{N}$ values of human blood are also useful indicators of dietary consumption patterns by using the omega-3 fatty acids docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) as an indication of fish ingestion. A study of a population of Yup'ik Eskimos with a uniquely high consumption of marine fish by O'Brien et al. (2009) found that red blood cell $\delta^{15}\text{N}$ values are correlated with both measured DHA and EPA levels and with self-reported measures of DHA and EPA intake in the diet. Positive correlations between $\delta^{15}\text{N}$ values and DHA/EPA intake were also found for hair samples collected from the same individuals, which could offer investigators a noninvasive, rapid, and relatively inexpensive method for monitoring omega-3 fatty acid levels in an individual (Nash et al., 2009).

14.19.6 Animal-Related (Nonhuman) Forensic Applications of Stable Isotope Analysis

14.19.6.1 Animal Migration and Movement

Stable isotope analysis has a long history in studies of non-human animals, traditionally for understanding dietary inputs. There has been a rapid expansion in the use of this technique to also understand animal movements in the past few decades. Rather than cover the nature of those advances here, we refer

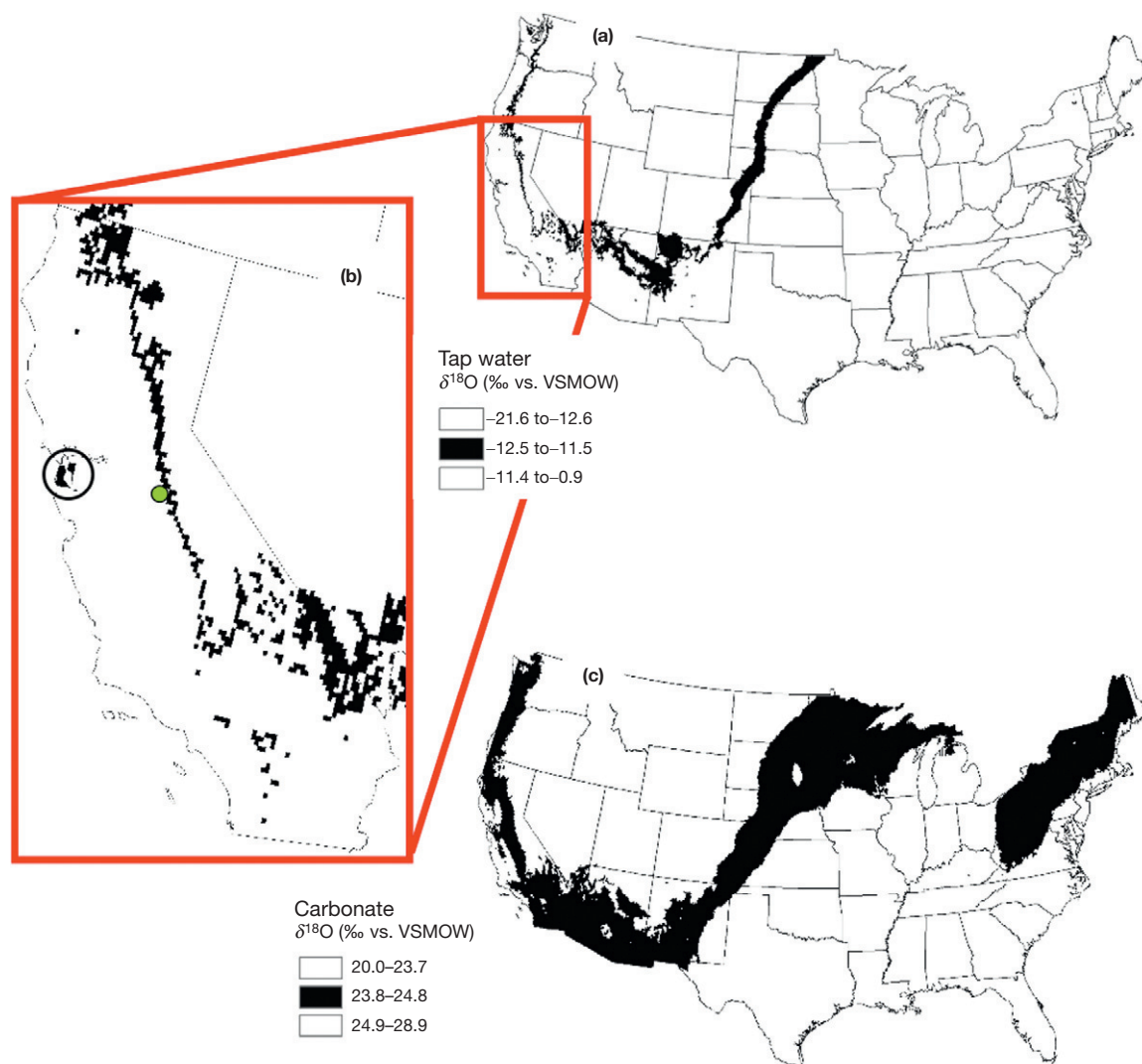


Figure 13 Possible regions of origin estimated for the oxygen isotope ratios measured in hair (a and b) and tooth enamel carbonate (c) from homicide victim 'Jane Doe.' Her remains were discovered in Stanislaus County, California, USA, shown by the green point in panel (b). Now identified as Mary Alice Willey, the victim was known to be living in the San Francisco Bay area, circled in panel (b), for a year prior to her death.

the reader to other published literature (Hobson, 1999; Hobson and Wassenaar, 2008; Rubenstein and Hobson, 2004; West et al., 2006a). The focus of this text is the use of stable isotope analysis to understand animal movement from a forensic angle, such as monitoring the international trade of animals, which is a primary goal of the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES, <http://www.cites.org/>).

One of the earliest examples of stable isotope analysis in wildlife forensics is in the investigation of butterfly origin, specifically monarchs (*Danaus plexippus*), to focus conservation efforts of natal grounds within the United States (Wassenaar and Hobson, 1998). Because the proteins in butterfly wings are metabolically inert after synthesis, the $\delta^2\text{H}$ values of wings collected from butterflies that died while wintering in Mexico were linked to the stable isotope ratios of water available in the location of wing development, hundreds of kilometers away in

the midwestern United States. Stable isotope analysis was also applied to investigate the cause of a sudden monarch population increase on the island of Cuba; the measured isotope ratios of the butterfly wings revealed many of the individuals in the newly expanded group likely originated from southeastern Canada or the northeastern United States and may have lost their way during migration (Dockx et al., 2004). More recently, the technique was applied on a smaller scale during research on the migration of peacock butterflies (*Inachis io*) in Sweden in an area of 200–300 km² (Brattström et al., 2008). Despite the more restricted range in geography – and thus in environmental isotope compositions – compared to the North American monarch work, a combination of stable isotope ratios ($\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ values) was useful for discriminating groups of butterflies with different natal origins. Measured $\delta^2\text{H}$ values of wing and chitin materials were used recently to investigate the origin of another insect in France – the hoverfly

Episyrphus balteatus, which is a natural predator of the common aphid crop pest (Ouin et al., 2011). In this study, the authors used hydrogen stable isotope ratio analysis not only to assign potential origin to hoverfly specimens but also to define the minimum separation distance necessary to distinguish regions of origin that differed due to latitude and the $\delta^2\text{H}$ value of precipitation.

Using a different metabolically inert tissue, feather keratin, it is possible to determine the isotopic composition of environmental water available to a bird during feather formation, which can reveal information about the origin of an individual (Chamberlain et al., 1997; Hobson et al., 2004; Rubenstein et al., 2002; see also Chapter 3 of Hobson and Wassenaar, 2008). While uncertainty in bird age and variability in the environmental water isotopes of an area can often only constrain region-of-origin predictions to broad zones (Langin et al., 2007; Wunder, 2010; Wunder and Norris, 2008b), these general predictions may nevertheless be enough to discriminate populations. Consider the successful ditching of US Airways Flight 1549 in the Hudson River in New York State on 15 January 2009, following a bird strike that disabled both engines. During an investigation of the incident, the National Transportation Safety Board found remains of Canada geese in both engines. In reaction, and to hopefully prevent any similar incidents, the city of New York oversaw the destruction of more than 3000 Canada geese adults and eggs in summer 2009. Yet hydrogen stable isotope ratio analysis of the feathers recovered from the engines revealed that the birds were likely part of a migrant flock and not local to the New York area after all (Marra et al., 2009).

14.19.6.2 Provenance of Trade Goods

A continuation of stable isotope analysis to understand the movements and migration patterns of animals in natural settings is its application to understand the economically motivated movements and trade of those animals (or animal tissues) prized by humans. In prehistoric settings the trade of animal-derived durable goods helped to encourage the development of local economies and complex societies. In modern settings the trade of animal-derived tissues like (misattributed) wool rugs and (illegally poached) ivory garner large profits for the perpetrators.

Despite the possible utility of stable isotopic composition to understand the distribution of shell beads from coastal sources to inland communities in prehistoric settings, there has been relatively little research on the subject. Most research has focused instead on the use of measured $\delta^{18}\text{O}$ values in shells to reconstruct prehistoric sea surface temperatures (e.g., Abell, 1985; Grossman and Ku, 1986; Thébault, 2007). However, collections of *Olivella biplicata* (Eerkens et al., 2005) and *Spondylus gaederopus* (Shackleton and Renfrew, 1970) shell beads have demonstrated that oxygen stable isotope ratio analysis can differentiate shells that originated from different coastal regions, providing important information on ancient trade routes. For example, Eerkens et al. (2005) determined that *O. biplicata* beads collected from archaeological sites in the interior of California, USA were likely sourced exclusively from the southern California coast, despite the fact *O. biplicata* is found along the entire coastline of California. In another

example, Shackleton and Renfrew (1970) found that *S. gaederopus* shell artifacts dateable to between 4000 and 2500 BC from an archaeological site in Bulgaria, near the Black Sea, were likely from the Aegean Sea and not the close-at-hand Black Sea as previously hypothesized.

Stable isotope analysis may also be useful to trace the origin of more modern trade goods, such as carvings made of ivory. Recently, a number of carved statues were seized in Kenya by customs authorities at Jomo Kenyatta airport. The origin of the carvings was unknown but, somewhat unusually, it was suspected that some of the statues could have been derived from hippopotamus ivory. Although smaller than elephant ivory, hippopotamus ivory can be used in carvings where it is passed off as elephant ivory. Previous work showed that ivory from different parts of Africa had different isotope ratio signatures, implying that isotope ratios could be used to determine ivory sources (van der Merwe et al., 1988, 1990; Vogel et al., 1990).

A stable isotope survey of elephant and hippo ivory in Kenya was completed on samples in the storage vault at Kenya Wildlife Service in Nairobi, and on other elephant and hippo remains collected in Kenya. Stable isotope analyses showed that certain regions within Kenya had limited $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ranges for bioapatite, and that hippopotamus ivory was distinct from elephant ivory (Cerling et al., 2007). Thus if the seized ivory carvings were from Kenya, it could be possible to ascertain from which region they were derived. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the carvings showed that most statues were unlike Kenyan ivory samples (Figure 14). Two seized statues were similar only to mountain regions of Kenya, where poaching of ivory is minor compared to other regions (especially in the eastern regions of the country). All samples were consistent with an origin in Central Africa, where elephants have very low $\delta^{13}\text{C}$ values, as may be expected in dense forest habitats. While it was not possible to go further in this investigation, especially without additional authentic samples from Central Africa for isotope comparison, future work may be able to extend this study using other isotopes, such as $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, or $^{234}\text{U}/^{238}\text{U}$ ratios, which have patterns determined in large part by surface geology.

The stable isotope analysis of wool – in raw form or as a woven fabric – has application for understanding trade in both modern and archaeological settings. Using samples gathered from modern flocks, several studies have found distinct differences in isotope signatures of wool related to the geographic origin, and possibly diet, of the animals (Frei et al., 2009; Hedges et al., 2005; Zazzo et al., 2011). In a study of sheep populations in Turkey, carbon and nitrogen isotope ratios in wool increased from coastal to inland grazing regions, while a continental pattern in measured $\delta^{34}\text{S}$ values was not as apparent despite the potential influence of marine sulfur deposition via the sea-spray effect (Hedges et al., 2005). On the other hand, a study of wool from a flock in Ireland did reveal a relationship between distance from the coast and measured $\delta^{34}\text{S}$ values; the relationship was strongest in animals on the west coast with the strongest prevailing winds (Zazzo et al., 2011). The only study published to date presenting the application of stable isotope analysis to ancient fabrics used Sr to characterize wool from different regions of the globe and then compared modern values to measured $^{87}\text{Sr}/^{86}\text{Sr}$ values for

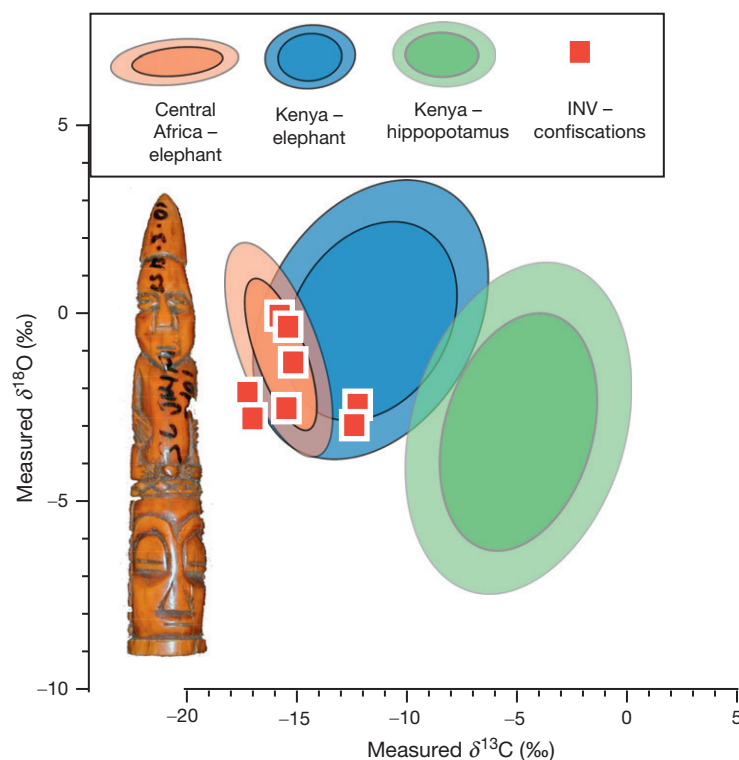


Figure 14 Measured oxygen and carbon isotope ratios of authentic elephant (red and blue circles) and hippopotamus (green circle) ivory, compared to ivory carvings seized in Kenya (squares). Some of the carvings were originally suspected to be hippopotamus ivory.

wool textiles discovered in Sweden and Denmark to determine how local – or not – the articles were (Frei et al., 2009).

14.19.7 Archaeological and Gem Origin Investigations Utilizing Stable Isotope Analysis

14.19.7.1 Sculpture Source: Monuments, Statues, and Artifacts

Stable isotopes have been used extensively to establish the provenance of historical artifacts and structural building materials used in antiquity. As with other materials of geologic origin, stable isotope compositions are related to the material type and history of its formation. In most archaeological studies investigating the geographic source of ancient building materials, stable isotopes alone cannot provide unequivocal evidence for a particular monument's material origins. Nonetheless, when used in combination with other chemical and physical characterization techniques, stable isotope analysis can provide an important piece of evidence for the source inference of a specimen.

As discussed previously for nonspatial forensic applications of isotope data, the archaeological investigation of a historical material's provenance requires extensive databases of authentic known-origin materials. In the case of building materials used in antiquity, a large body of stable isotope data has been compiled for historic quarry sites and the geochemistry of the quarried rock (Attanasio et al., 2006; Brilli et al., 2010; Galan et al., 1999; Gorgoni et al., 2002; Herz and Dean, 1986; Lapuente et al., 2000). These baseline data provide the

foundation for comparison between an historical structure and potential source quarries or regions (Akarish and Dessandier, 2011; Antonelli et al., 2003; Attanasio et al., 2008; Brilli et al., 2011; De Vito et al., 2004; Pinter et al., 2004). In addition to structural materials, the comparison of stable isotope measurements and databases has also been used to understand the region of origin of jewelry (Hull et al., 2008) and glass artifacts (Henderson et al., 2005; Silverstri et al., 2010), which is discussed in more detail in Chapter 14.14. However, in the haste to analyze archaeological materials during investigations the necessity of a detailed database foundation is often overlooked and points to a continuing need for the acquisition of authentic material of known origin for comparison (Beardsley and Goles, 2001).

The marble of the David sculpture by the artist Michelangelo illustrates the applicability of stable isotope analysis to establish the provenance of the material used to produce significant artifacts (Attanasio et al., 2005). Michelangelo was the third sculptor commissioned to create a statue from the block of marble that ultimately produced the David. While the progression of the sculpting process was well documented, little information exists about where the block of marble was quarried. Given the destructive nature of isotope analysis, samples of the David were difficult to acquire. Relatively recently a specimen was made available from a recovered portion of the sculpture that was damaged by an act of vandalism. Using stable carbon and oxygen isotope analyses in combination with spectroscopic and petrographic examination, the marble used to create the David statue was identified as being from a single quarry site within Carrara, a large marble-producing

region in Italy (Attanasio et al., 2005). A broader discussion of the authentication of marble beyond this case example is presented in Chapter 14.16.

14.19.7.2 Gem Origins

Stable isotope analyses have proven useful for determining the provenance of precious and semiprecious gems, particularly when used in combination with traditional gemological techniques (i.e., refractive index, birefringence, density, etc.). The rarity and specific geologic occurrence of a gem are important characteristics that lend value to a particular gemstone along with size, cut, and clarity (Rossman, 2009). Thus, there are clear financial incentives for unscrupulous vendors to falsely claim a gem is from a certain region and for honest vendors to certify a gem's true origin. Recent advances in isotope sampling and measurement techniques, like laser ablation, have greatly expanded the application of nondestructive analysis of gem quality and historically significant gems for certification and investigative purposes.

14.19.7.2.1 Rubies and sapphires

Rubies and sapphires are the same mineral (corundum, Al_2O_3) and only vary in color due to varying amounts of the trace elements chromium, iron, titanium, and vanadium. Gemologic and trace element measurement techniques can be used in many cases to identify a ruby or sapphire crystal's specific geologic and geographic origin (Rankin et al., 2003). For excellent gem-quality rubies and sapphires that have only limited imperfections and inclusions, stable oxygen isotope measurements can provide an additional means to establish a gemstone's origin. The $\delta^{18}\text{O}$ values of corundum gems range from 2.9 to 23.0‰ and reflect the geologic environment of formation, whereby $\delta^{18}\text{O}$ variations in a gem are related to the isotopic composition of the hydrothermal fluids in which the gem precipitated (Giuliani et al., 2005; Yui et al., 2003). In turn, the $\delta^{18}\text{O}$ values of the hydrothermal fluids are derived from the isotopic composition of the host rock, the amount of rock–fluid interaction, and the temperature of the reaction (Giuliani et al., 2000). The $\delta^{18}\text{O}$ values of rubies and sapphires are not affected by artificial heating (which serves to enhance gem color) and measured oxygen isotope ratios can thus closely reflect the geological source and geographic region of origin of gem-quality stones (Giuliani et al., 2005). Furthermore, highly prized sapphires from Kashmir, Madagascar, and Sri Lanka have distinctive $\delta^{18}\text{O}$ values that, when combined with the quantification of other physical properties, offer a powerful forensic fingerprint of gem origin (Giuliani et al., 2005, 2007).

14.19.7.2.2 Emeralds

Emeralds are gem-grade green beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$), rarer than diamonds, and measured $\delta^{18}\text{O}$ values have been promoted as a method to establish an emerald's provenance (Giuliani et al., 1998; Zwaan et al., 2004). The $\delta^{18}\text{O}$ values of emeralds range from 6.2 to 24.7‰ and reflect the geologic environment in which the gems were deposited (Fallick and Barros, 1987; Giuliani et al., 2000; Zwaan et al., 2004). Based on $\delta^{18}\text{O}$ values, emeralds can be classified into three categories that correspond to the type of emerald deposit: (1) 6.2–7.9‰, (2)

8.0–12‰, and (3) >12‰. Within these categories, emeralds from a single deposit have narrow $\delta^{18}\text{O}$ ranges that typically span less than 1‰ (Giuliani et al., 2000; Zwaan et al., 2004) and, when combined with other gemologic properties, this categorization allows for specific deposits to be identified as the origin of a particular gem. This technique has been applied to identify the origin of several historically significant emeralds and establish the trade routes that these gems followed (Giuliani et al., 2000). We note that in addition to the precious gems, rubies, sapphires, and emeralds, the measured $\delta^{18}\text{O}$ values of semiprecious gems can also distinguish region of origin in combination with other elemental analyses (Giuliani et al., 2011).

14.19.7.2.3 Diamonds

Diamonds are predominately carbon with minor trace impurities. Diamond carbon isotope compositions ($\delta^{13}\text{C}$) range between −38.5 and 5.0‰, with the vast majority having values between −8 and −2‰ (Cartigny, 2005). While carbon isotope values of diamonds do not relate to specific geologic occurrences, sulfur and nitrogen isotopes ratios can differentiate diamond types (Cartigny, 2005). Unlike other precious gemstones, it may not be possible to isolate individual geographic origin localities using the stable isotope fingerprints of diamonds alone (Palot et al., 2009).

14.19.8 Isotope Geochemists as Contributors to the Forensic Sciences

14.19.8.1 Addressing the Needs of the NRC Report

In 2009, the National Research Council of the United States released a highly anticipated review of the nation's forensic sciences system. The report not only included a summation of the main areas of deficiency in the community but also a list of suggested policy changes and procedure reforms (NRC, 2009). Two of the main concerns highlighted in the report were (1) the underdeveloped scientific basis for some commonly applied forensic techniques, like bite mark and fingerprint analysis; and (2) a lack of understanding and acknowledgment of the uncertainties associated with different analytical techniques.

The stable isotope analysis techniques used by isotope geochemists have the capability to address some of the most pressing needs noted in the National Research Council's report *Strengthening Forensic Science in the United States: A Path Forward* (NRC, 2009). As discussed in this chapter, stable isotope analysis techniques like those often employed in isotope geochemistry research have been and will likely continue to be an important contributing tool in forensic investigations. Perforce, the isotope geochemist as a stable isotope analyst may be a crucial provider of evidence in both active investigations and the courtroom. Providentially, stable isotope evidence has a strong scientific basis and the academic community has exhaustively reviewed many of the methods used by isotope geochemists to prepare samples and measure stable isotope ratios. By nature the measurements collected using these methods are quantitative, independent, and repeatable and are therefore well suited to additional peer review and validation.

Expanding on its application in the academic realm, the use of stable isotope analysis in the forensic science community has been accompanied by an effort to identify and understand the impact of uncertainty during data interpretation. The near-universal availability and use of reference materials during stable isotope analyses allows the analyst to easily provide an estimate of the uncertainty associated with measurements. Several recently published texts have attempted to guide the analyst in using this uncertainty to generate a probability ('likelihood') of origin assignment (Wunder, 2010; Wunder and Norris, 2008a,b). While the probabilistic approach has primarily focused on animal migration, it has also been applied in forensic cases involving collected specimens of explosives (Pierrini et al., 2007) and paint (Farmer et al., 2009b). A recent study on human drinking water and hair isotopic compositions by Kennedy et al. (2011) further developed the likelihood approach in a forensic setting. Using combinations of uncertainty estimates, the authors demonstrated that different assumptions led to different conclusions on the strength and specificity of predicted origins (Kennedy et al., 2011), an important factor to acknowledge when presenting data in a forensic case.

14.19.8.2 Isotopes in the Courts

Despite the suitability of stable isotope signatures as forensic evidence, to date and to the best of our knowledge no isotope data have been presented in the US courts. However, the ever-increasing use of stable isotope analyses in forensic investigations (Benson et al., 2006; Meier-Augenstein, 2010) means it is likely only a matter of time until stable isotope ratios are used in a legal setting in the United States. At that time, it will be incumbent upon the court to rule on the admissibility of the evidence as it pertains (or not) to the matter at hand. In anticipation of this event, Ehleringer and Matheson (2010) published an article to aid both counsel and court on the use of stable isotopes in the legal system, with the hope of assisting the law community while simultaneously demonstrating how stable isotope analysis generates the empirical evidence needed by the forensic science community.

Introducing scientific evidence in a court of law via the use of expert testimony is only possible if both the evidence and testimony have been evaluated for reliability and validity by the presiding judge, a precedent that was established in 1993 by the landmark US Supreme Court case *Daubert versus Merrell Dow Pharmaceuticals, Inc.* (Ehleringer and Matheson, 2010). When considering the admission of scientific evidence, a judge must consider several aspects of the evidence including the general acceptance of the scientific approach, its testability, its level of peer review, the known error rate of the analytical method, and whether or not standards exist for data evaluation (Bell, 2009). Several features of the good scientific methods practiced by isotope geochemists make isotope data ideally suited for this scrutiny, including the standardized handling of samples, use of peer-reviewed preparation protocols and analytical methods, and established models for applying statistics and interpreting data.

14.19.8.3 Concluding Points

A surge of recent publications describing the investigative use of stable isotope analysis highlights the expansion of this

technique into the forensic community from its inception in the academic community (Benson et al., 2006; Ehleringer et al., 2007; Meier-Augenstein, 2010). While the application of stable isotope measurements is well understood in fields like ecology and geochemistry (Fry, 2006; Sharp, 2006), its applicability in forensic investigations is still being established. Stable isotope signatures are just the type of numerical and empirical evidentiary data that are required by the forensic science community (NRC, 2009) and, as such, we feel it is only a matter of time before stable isotope analysis is a routine method employed in investigations and presented in a court of law (Ehleringer and Matheson, 2010). To prepare for this possibility, recent publications have focused on helping both stable isotope analysts and forensic investigators develop a suitable framework for the application of stable isotope analysis (Ehleringer et al., 2007, 2010; Gentile et al., 2011). In this chapter, we have described a framework that can be easily adopted by the stable isotope geochemist.

The utility of the framework presented here lies within its flexibility. An investigator may be interested in answering not just one but a series of questions related to an evidence specimen and the complexity of those questions will vary based upon the material type and what is known or not about the collected sample (see Figure 1). We have presented examples of how stable isotope analysis has been – and can be – applied to both nonbiological and biological materials to answer comparative and predictive forensic questions at both nonspatial and spatial scales. Examples of the materials include illicit drugs, mixed explosives and explosive reagents, packaging materials, petroleum products, water and other water-based beverages, tissues from plants and animals, adulterated food items, ancient building materials, and precious minerals. Yet the examples discussed in this chapter only represent a small portion of the ways in which stable isotope analysis can be applied in forensic investigations. The novel application of stable isotope measurements to additional types of materials in the future will no doubt be extremely exciting, especially considering the additional information a stable isotope fingerprint can potentially add to the forensic investigation of a specimen.

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