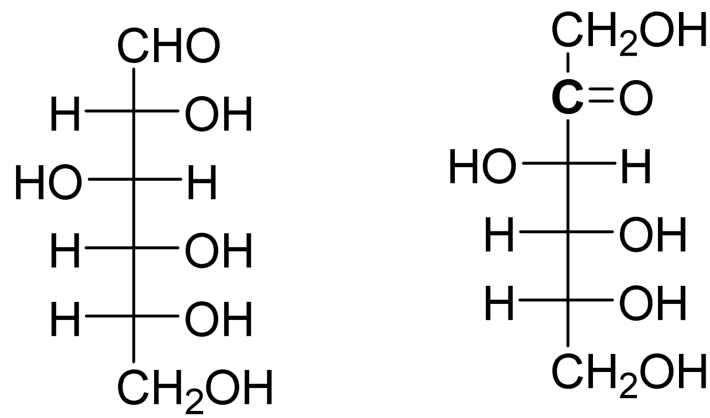
Carbohydrates

- Molecular formula has the form $C_x(H_2O)_y$ (a "hydrate of carbon")
- **Monosaccharides** ("simple sugars) are the basic building blocks of carbohydrates. They have a single contiguous chain of carbon atoms and a formula of $C_nH_{2n}O_n$.
- One common way of depicting sugars is with Fischer projection. If a carbonyl is present, that end is on the top end of the Fischer projection:

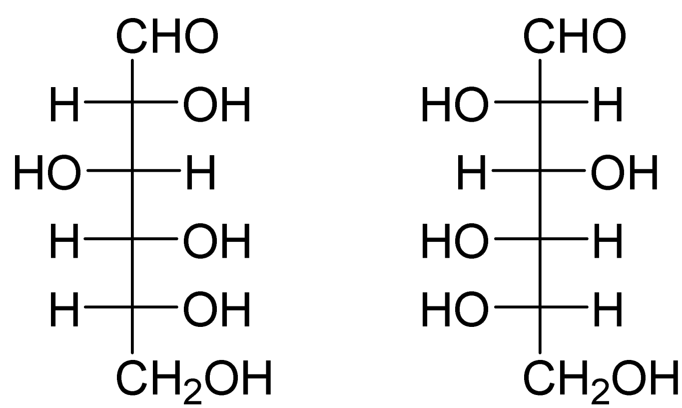


glucose fructose

//

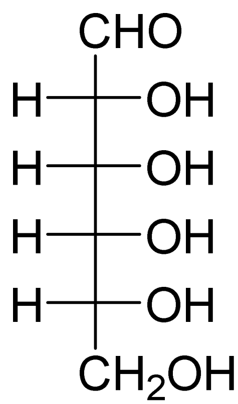
Carbohydrate Stereochemistry

- D- vs. L- sugars: if the hydroxyl nearest the $–CH_2OH$ group in the Fischer projection is on the right, the structure corresponds to a D-sugar. If it's on the left, the structure represents an L-sugar.
- Most sugars in nature are D-sugars.
- D- and L- here do NOT correspond to rotation of plane-polarized light (*d/l* or +/-).

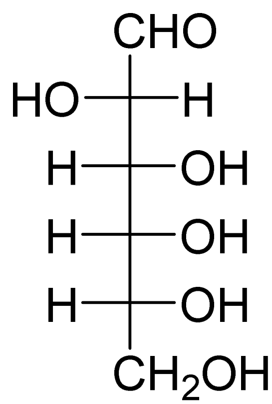


D-glucose L-glucose

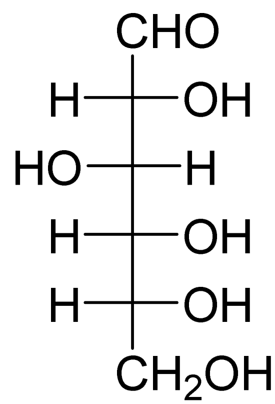
- All other stereochemistry relative to the bottom-most –CHOH group (the one that determines D- vs. L-) is indicated by the name of the sugar.



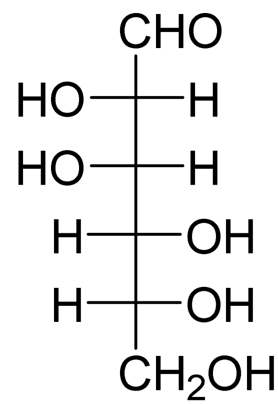
D-allose



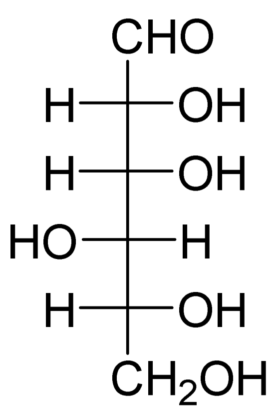
D-altrose



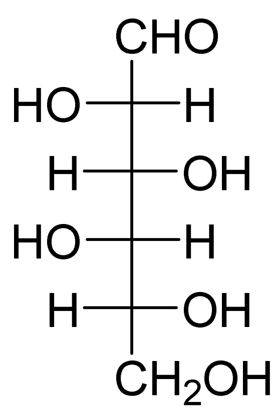
D-glucose



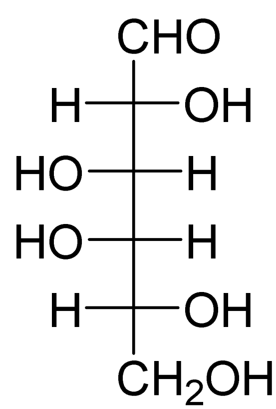
D-mannose



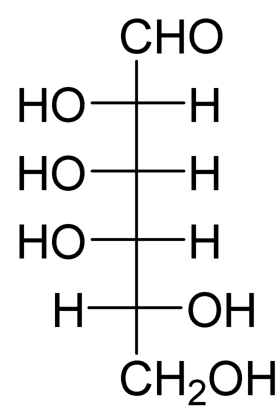
D-gulose



D-idose



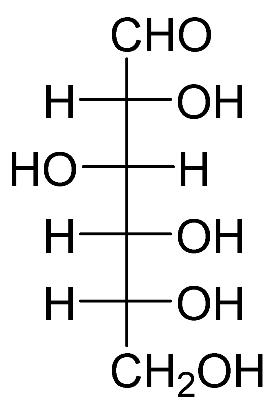
D-galactose



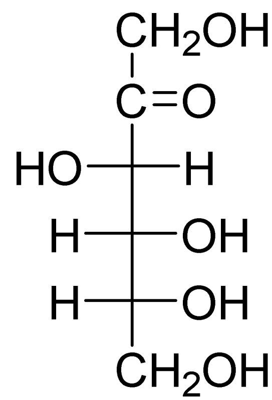
D-talose

Carbohydrate Terminology

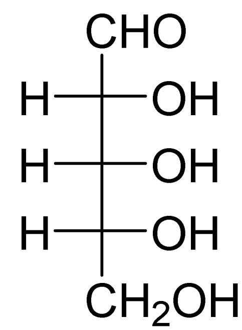
- Aldose/Ketose: If the sugar is an aldehyde, it is an **aldose**. If it is a ketone, it is a **ketose**.
- The number of carbons in a sugar can be described by using a numerical prefix followed by –ose: e.g. triose, tetrose, pentose, hexose for 3, 4, 5, and 6 carbons respectively.
- These can be combined by using “aldo-” or “keto-” as a prefix: ketohexose, aldopentose, etc.



glucose
an aldohexose



fructose
a ketohexose



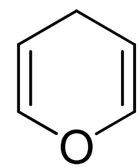
ribose
an aldopentose

- Also try problem 22.8 a, b, d

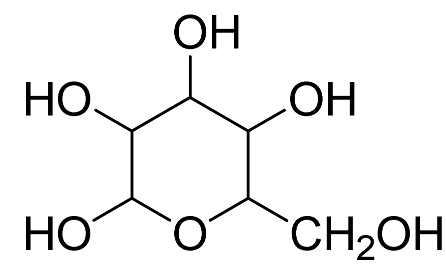
Sugar Hemiacetals

- Sugars are at equilibrium between open-chain and cyclic hemiacetal forms, favouring the latter.

•Aldohexoses have a strong preference for the **pyranose** form (the 6-membered ring) over the **furanose** form (the 5-membered ring).

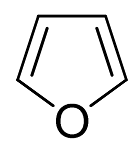


a pyran

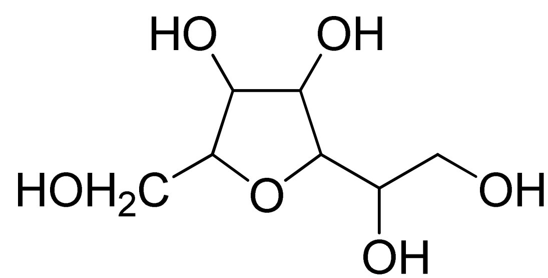


an aldohexose
in its pyranose form

•A specific sugar hemiacetal can be referred to by using the sugar's name as a prefix (e.g. gluco- for glucose) followed by "pyranose" or "furanose"



furan

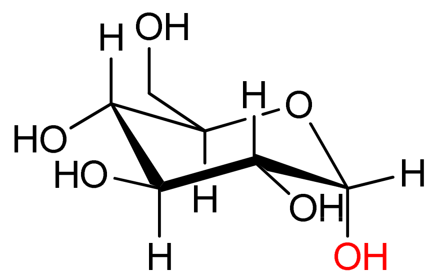


an aldohexose
in its furanose form

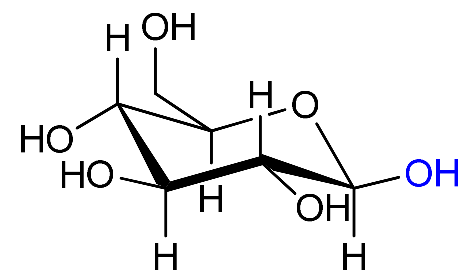
α- and β- Anomers

- **Anomers** refer to two sugars that differ only by the stereochemistry at the carbon which is the carbonyl carbon in the open-chain form (the "**anomeric carbon**").

Chair structure:
α-OH axial, β-OH equatorial

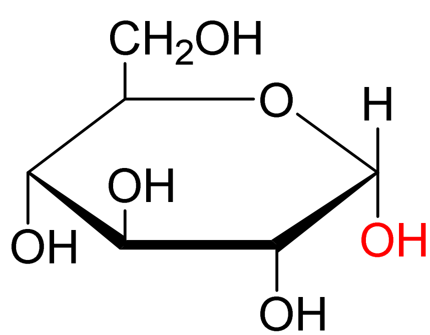


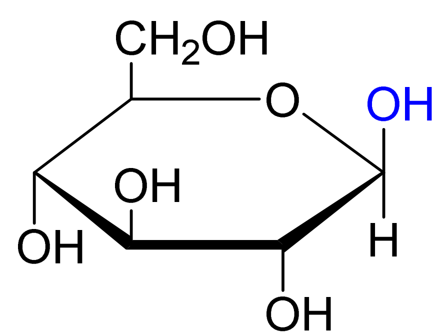
α-D-glucopyranose



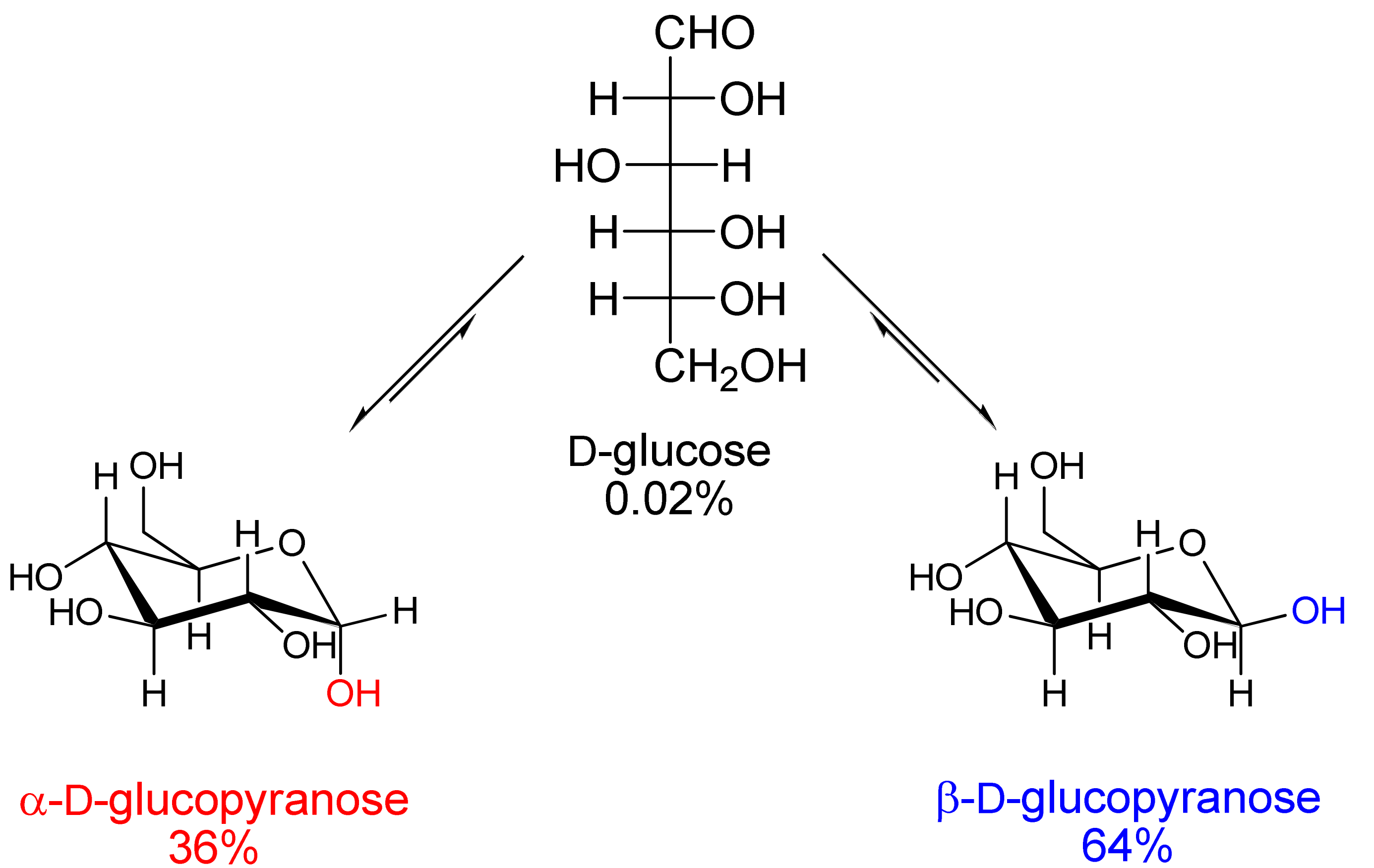
β-D-glucopyranose

"Haworth" structure:
α- down, β-up





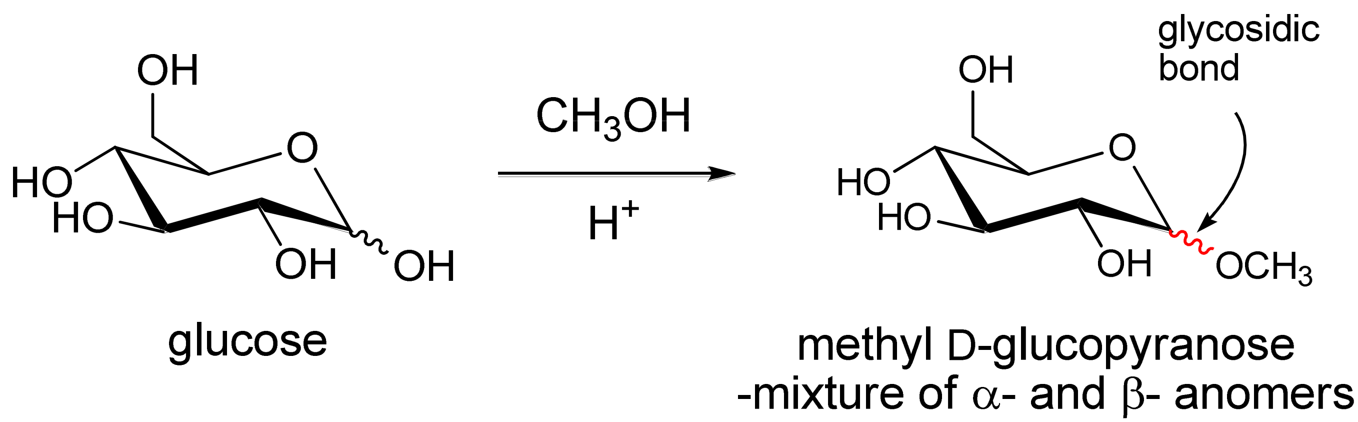
α- and β- anomers of cyclic hemiacetals interconvert via the open-chain aldehyde.



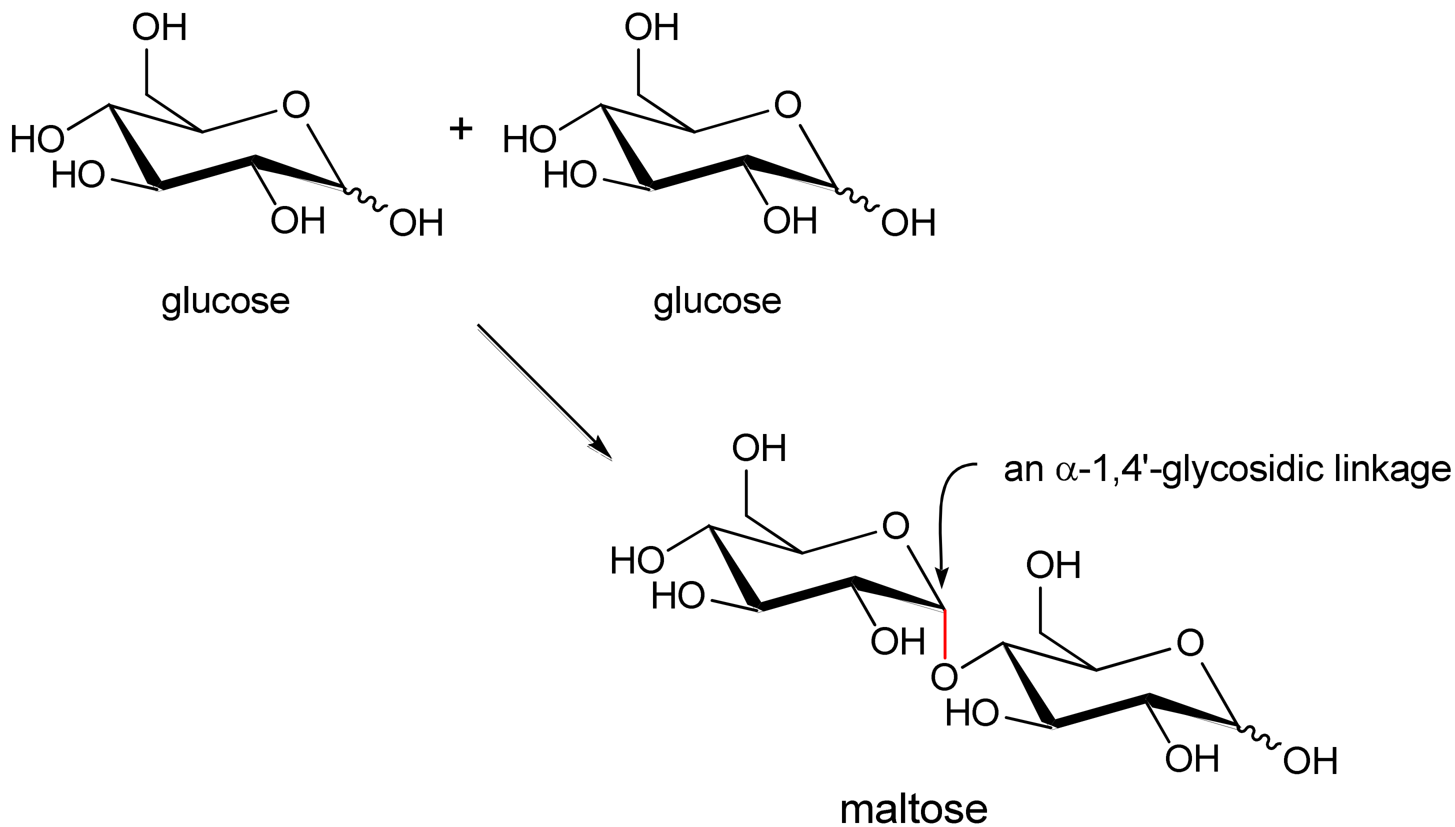
See text, p. 1236.

Glycosides

- A monosaccharide hemiacetal can react with an alcohol to form an acetal. Such acetals are called **glycosides**, and the new C-O bond is called a **glycosidic bond**.

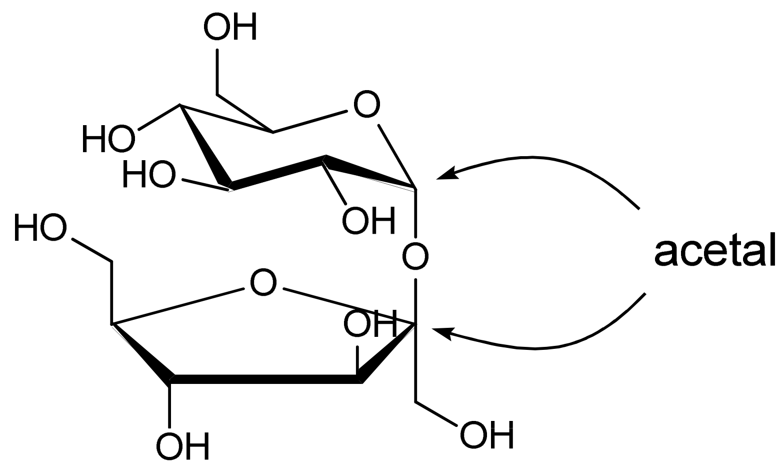


•When the alcohol is another monosaccharide, formation of a glycoside between the two gives a **disaccharide**:



•The remaining aldehyde/hemiacetal carbon of maltose can in theory be reduced to a $–CH_2OH$ group (e.g. with $NaBH_4$). Such sugars are called **reducing sugars**.

•Sucrose (table sugar) is a disaccharide of glucose and fructose:



sucrose

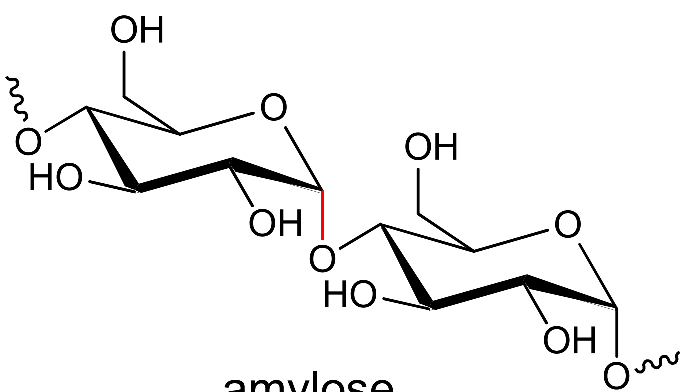
•Because both sugars have made a glycosidic linkage between their anomeric carbons, there is no hemiacetal functionality remaining. Fructose is an example of a **nonreducing sugar**.

Polysaccharides

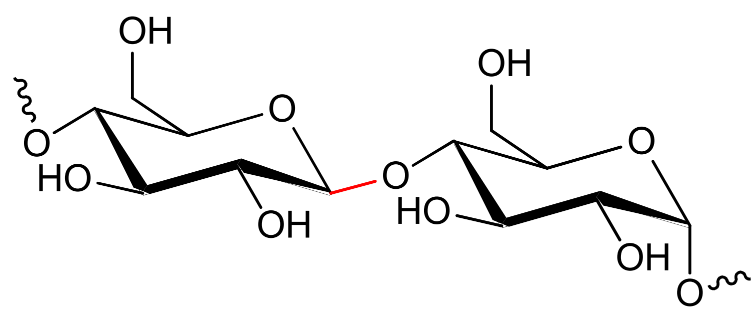
- Carbohydrates with a known, small number of subunits can be referred to as disaccharides, trisaccharides, etc.
- The term **oligosaccharide** refers to sugars constructed from ~3-10 monosaccharide units. Larger molecules are referred to as **polysaccharides**.
- Polysaccharides include cellulose, starches such as amylose and amylopectin (used by plants to store glucose) and glycogen (used by animals and humans to store glucose).

Cellulose and Amylose

- The only difference between cellulose (which humans can't digest) and amylose (a starch which we can digest) is the glycosidic linkage between glucose subunits.



amylose
(α-1,4'-glycosidic linkage)



cellulose
(β-1,4' linkage)

spaghetti

The box spaghetti comes in

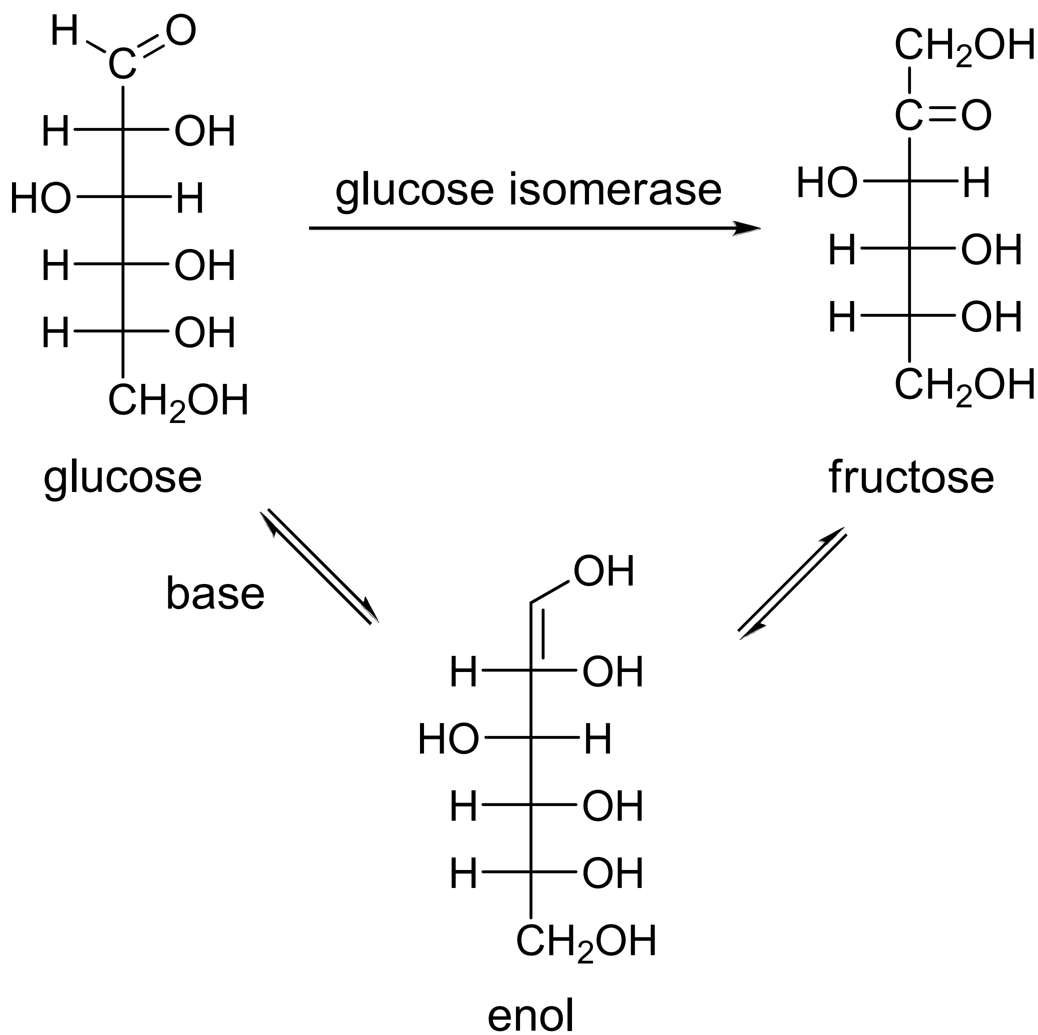
High-Fructose Corn Syrup (HFCS)

- Recall sucrose is a disaccharide of glucose and fructose.
- Fructose is over twice as sweet as glucose.

- Corn syrup is made from enzymatic breakdown of corn starch to glucose and glucose-containing oligo-saccharides.

- Although corn syrup contains no fructose, its glucose can be converted enzymatically to fructose. The most common grades of HFCS are roughly 1:1 glucose:fructose. A 45:55 ratio has the same sweetness as sucrose, and is commonly used in soft drinks.

Glucose and fructose are tautomers of each other that can interconvert with base via the enol, as well as via enzymatic isomerization:



Is HFCS Unhealthy?

- Short answer: about as unhealthy as sucrose. HFCS is essentially what our body produces when it hydrolyzes sucrose to glucose and fructose. Fructose is also naturally found in many foods, including fruits and honey. Carbohydrates in general are sources of calories, and HFCS added to processed foods will increase their caloric content.

- Longer answer: there may be reasons for HFCS to have a higher impact on obesity and diabetes, but nothing conclusive has been found. The main problem with HFCS is that it makes it easy to add calories to our diet.

The Rise of Corn

- Corn is the largest grain crop in the world by mass (780 million tonnes in 2007).
- Corn has the highest yields of any grain (5 tonnes/hectare).
- Corn can be used as a source of fats and protein as well as carbohydrate
- Corn is a fungible commodity

http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor

"Corn Chips With Legs"

- Corn is one of the few crops that use C4 carbon fixation for photosynthesis. Most plants are C3, but suffer in hotter and drier climates because of an undesirable side-reaction called photorespiration.

- C4 plants take up more ^{13}C from the atmosphere than C3 plants do. Measuring the relative amount of ^{13}C in a food, animal or person correlates to how much of that carbon originally came from corn.

"When you look at isotope ratios, we North Americans look like corn chips with legs."

--Todd Dawson. From *The Omnivore's Dilemna* by M. Pollan.

Example: McDonald's

- Pollan had a McDonald's meal analyzed by mass spectrometry. The percent of carbon in each foodstuff that was derived from corn was then calculated:

Soda: 100%

Milkshake: 78%

Salad Dressing: 65%

Chicken Nuggets: 56%

Cheeseburger: 52%

French fries: 23%

From *The Omnivore's Dilemna* by M. Pollan.

Corn as a Raw Material

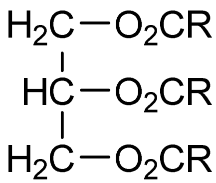
Corn can be refined or chemically modified into a variety of foodstuffs and materials:

- Carbohydrates (corn syrup, starch, HFCS, corn meal)
- Amino acids (from gluten and from fermentation)
- Fats and oils (corn oil, margarine, shortening)
- Ethanol
- Food additives (vitamins, xanthan gum, citric acid, MSG)
- Plastics

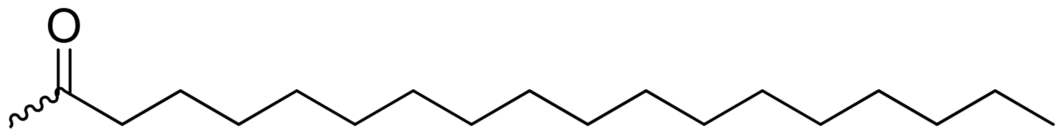
Less than 10% of the corn crop is used directly for human consumption! The bulk of it is used for animal feed, ethanol production and industrial materials.

http://www.ers.usda.gov/AmberWaves/February08/Features/CornPrices.htm

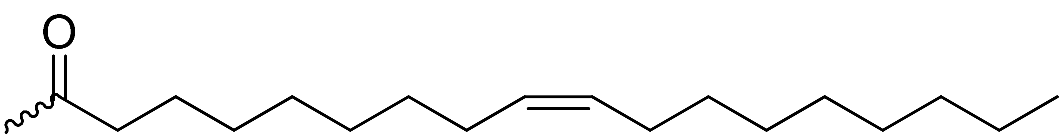
Fats and Oils



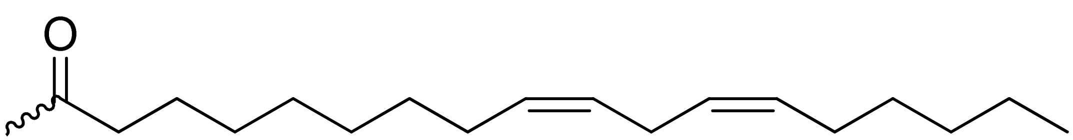
Recall that a fat is a triester of glycerol:
a **triacylglyceride**



Saturated fats have no C=C double bonds in the fatty acid sidechains



Natural unsaturated fatty acids contain a cis-double bond.



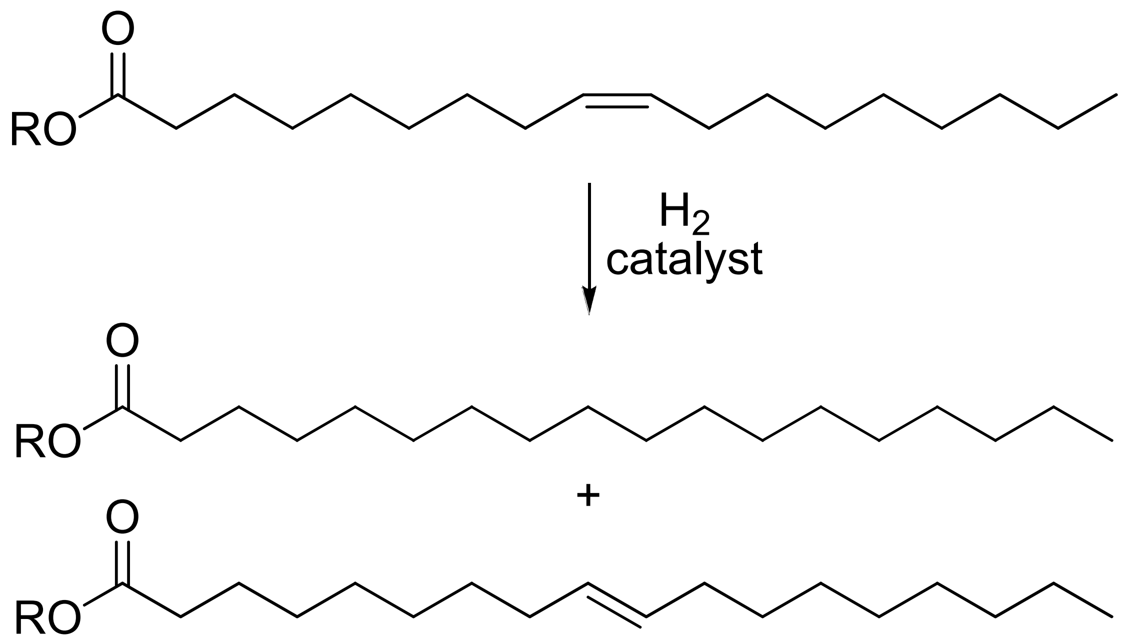
Polyunsaturated fatty acids contain multiple double bonds.

Hydrogenated Vegetable Oil

- Saturated fats tend to be solids at room temperature. Unsaturated fats have lower melting points and tend to be oils at room temperature. This is because the “kink” introduced in a fatty acid chain by the cis-double bond causes the molecules to pack less tightly together.
- Vegetable oils can be partially or completely hydrogenated using H_2 and a metal catalyst to give a fat with a certain desired consistency (e.g. margarine, shortening).

trans- Fats

- In the process of hydrogenation, some of the natural *cis*-fatty acid sidechains are converted to unnatural *trans*-fatty acids:



•Research is revealing that these *trans*-fats, which previously were counted as “unsaturated fat” on nutritional labels, are as bad as saturated fats, or even worse for your health. Nutritional labels now show trans-fats as a separate category.

“In clinical studies, TFA or hydrogenated fats tended to raise total blood cholesterol levels. Some scientists believe they raise cholesterol levels more than saturated fats. TFA also tend to raise LDL (bad) cholesterol and lower HDL (good) cholesterol when used instead of cis fatty acids or natural oils. These changes may increase the risk of heart disease.

Because there are no standard methods, it's difficult to estimate the TFA content of food items. It's also difficult to estimate intake, especially long-term intake…. As of January 2006, the FDA requires *trans* fat to be listed on the nutrition label. Although changes in labeling are important, they aren't enough. Many fast foods contain high levels of TFA. There are no labeling regulations for fast food, and it can even be advertised as cholesterol-free and cooked in vegetable oil. Eating one doughnut at breakfast (3.2 g of TFA) and a large order of french fries at lunch (6.8 g of TFA) add 10 grams of TFA to one's diet, so the lack of regulations for labeling restaurant foods can be harmful to your health”

-American Heart Association (www.americanheart.org)

“The American Heart Association's Nutrition Committee strongly advises these fat guidelines for healthy Americans over age 2:

- Limit total fat intake to less than 25–35 percent of your total calories each day;

- Limit saturated fat intake to less than 7 percent of total daily calories;

- Limit *trans* fat intake to less than 1 percent of total daily calories;

- The remaining fat should come from sources of monounsaturated and polyunsaturated fats such as nuts, seeds, fish and vegetable oils; and

- Limit cholesterol intake to less than 300 mg per day, for most people. If you have coronary heart disease or your LDL cholesterol level is 100 mg/dL or greater, limit your cholesterol intake to less than 200 milligrams a day.

For example, a sedentary female who is 31–50 years old needs about 2,000 calories each day. Therefore, she should consume less than 16 g saturated fat, less than 2 g *trans* fat and between 50 and 70 grams of total fat each day (with most fats coming from sources of polyunsaturated and monounsaturated fats, such as fish, nuts, seeds and vegetable oils).”

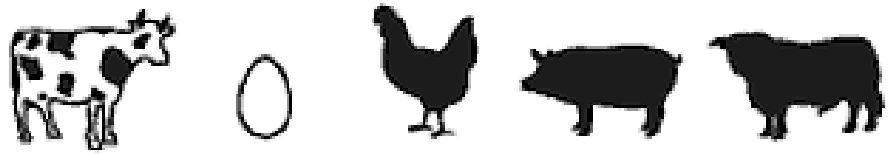
-American Heart Association (www.americanheart.org)

Meat Production

- An abundance of inexpensive crops such as corn and soy has allowed the production of inexpensive meat.

- Because livestock are higher up the food chain, a large amount of our crops are directed towards meat production instead of human consumption. For example, 55% of the U.S. corn crop is used in animal feed.

- Beef production is particularly inefficient at converting feed to protein.

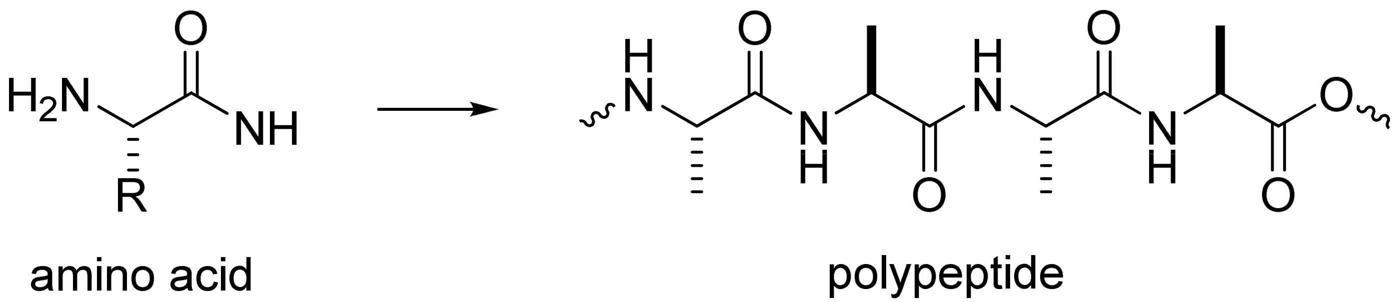


	milk	eggs	chicken	pork	beef
feed conversion (kg of feed/kg of live weight)	0.7	3.8	2.3	5.9	12.7
feed conversion (kg of feed/kg of edible weight)	0.7	4.2	4.2	10.7	31.7
protein content (% of edible weight)	3.5	13	20	14	15
protein conversion efficiency (%)	40	30	25	13	5

Source: *Energy in nature and society* by Vaclav Smil (2008)

Amino Acids

- **Amino acids** are the basic building blocks of proteins. A protein is a polymer made from amino acids connected primarily by amide linkages.



- There are 20 different amino acids. 9 of these cannot by synthesized by humans and must be obtained in the diet. These are called **essential amino acids**.

Complete Proteins

- Meat provides all the essential amino acids humans need—it is a **complete protein.**
- Most plant sources are deficient in one or more essential amino acids (**exception: soy protein**). For example, corn is low in lysine and tryptophan.
- However, different plant sources can be combined to provide a complete protein (e.g. rice and beans).

http://www.nlm.nih.gov/medlineplus/ency/article/002467.htm#Food%20Sources

Agriculture's Energy Cost

- Up to 20 percent of fossil fuel consumption in the U.S. is directed towards food production.
- Pollan gives the following estimates for fossil fuel consumption:

  0.3 gal oil per bushel corn

  35 gal oil per steer
- About 1/3 of this energy is used to produce fertilizer alone.

http://edition.cnn.com/2008/WORLD/asiapcf/03/16/eco.food.miles/

The Omnivore's Dilemna by M. Pollan.

Nitrogen Fixation

- In nature, nitrogen gas is converted to other sources of plant-accessible nitrogen (nitrates, etc.) by bacteria (e.g. the symbiotic bacteria in legumes) and (to a much smaller extent) lightning. This conversion is called **nitrogen fixation**.

- Human agriculture requires more fixed nitrogen than nature provides. One researcher estimates that 2/5ths of the world's population would not exist were it not for synthetic fertilizer.

The Omnivore's Dilemna by M. Pollan.

The Haber Process

- The **Haber Process** is an energy-intensive method to convert nitrogen and hydrogen gases to ammonia, which can then be used directly or indirectly as fertilizer.

  - $N_2 + 3\ H_2 \rightarrow 2\ NH_3$

- High temperatures and pressures are required, as well as a source of hydrogen gas. All this requires a lot of energy.

Consequences of Productivity

- Abundance of corn/soy etc → abundance of meat
- Highly productive farmers, plus gov't subsidies, mean that basic staples are cheap. Profit is in "value added" processed foods. People pay extra for features such as: convenience (microwavable entrees), taste (e.g. artificial flavours), entertainment value (kid's cereal).
- The ability to recombine refined carbs, proteins and fats into foodstuffs results in cheap, calorically-dense foods.
- The "inelasticity of consumer demand" (how much a person can eat) actually has some elasticity –the elastic waistband.

Walking a Dietary Minefield

Processed foods, plus cheap meat and dairy, encourage creating high-energy food that people will enjoy eating. Here are a few examples of foods that pack more calories and fat than you might expect.

Starbuck's Venti Java Chip Frappucino:
600 cal (23g fat, 14g sat'd, 0.5g *trans*-)

½ lb lean meatloaf: 410 cal (11 g fat, 4.4g sat'd fat)

Starbuck's skim latte: 130 cal (0g fat)

McDonald's Triple-Thick Chocolate Shake (32 oz):
1160 cal (27g fat, 16g sat'd, 2g *trans*-)

Ruby Tuesday's Entrees, ca. 2007:
http://www.cspinet.org/nah/03_07/xtreme.pdf

Colossal Burger: 1,940 cal, 141 grams fat --"Maybe I should have the white meat chicken and steamed broccoli penne pasta? That sounds healthy…"

…2,060 cal, 128g fat.

D'oh!

Uno's Pizza Skins Appetizer:

PIZZA SKINS			
Serving Size(g)	144g	Servings	5
Calories	480	Calories from Fat	280
% Daily Value*, Calories:		2,000	2,500
Total Fat	31g	48%	39%
Saturated Fat	9g	45%	36%
Trans Fat	0g		
Cholesterol	35mg	12%	12%
Sodium	720mg	30%	30%
Total Carbohydrates	39g	13%	10%
Dietary Fiber	2g	8%	7%
Sugars	2g		
Protein	13g		

Vitamin A 8% • Vitamin C 6% • Calcium 20% • Iron 10%

*Percent Daily Values are based on 2,000 and 2,500 calorie diets. Your daily values may be higher or lower depending on your calorie needs:

Calories:		2,000	2,500
Total Fat	Less Than	65g	80g
Saturated Fat	Less Than	20g	25g
Cholesterol	Less Than	300mg	300mg
Sodium	Less Than	2,400mg	2,400mg
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

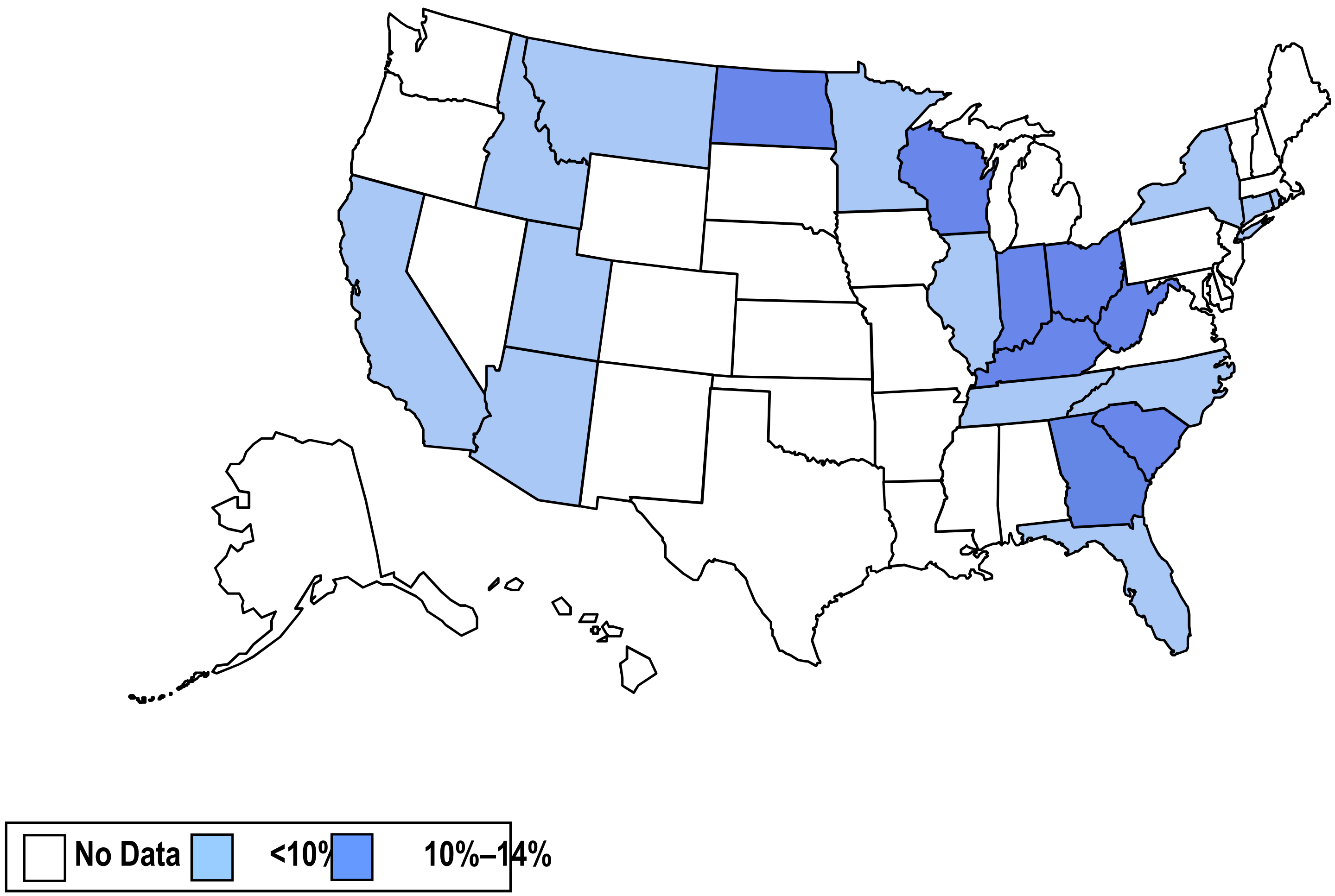
What's the catch?

2,400 cal, 155g fat, 45g saturated fat (over 2 days' worth)—BEFORE your pizza even arrives!

Obesity Trends* Among U.S. Adults

BRFSS, 1985

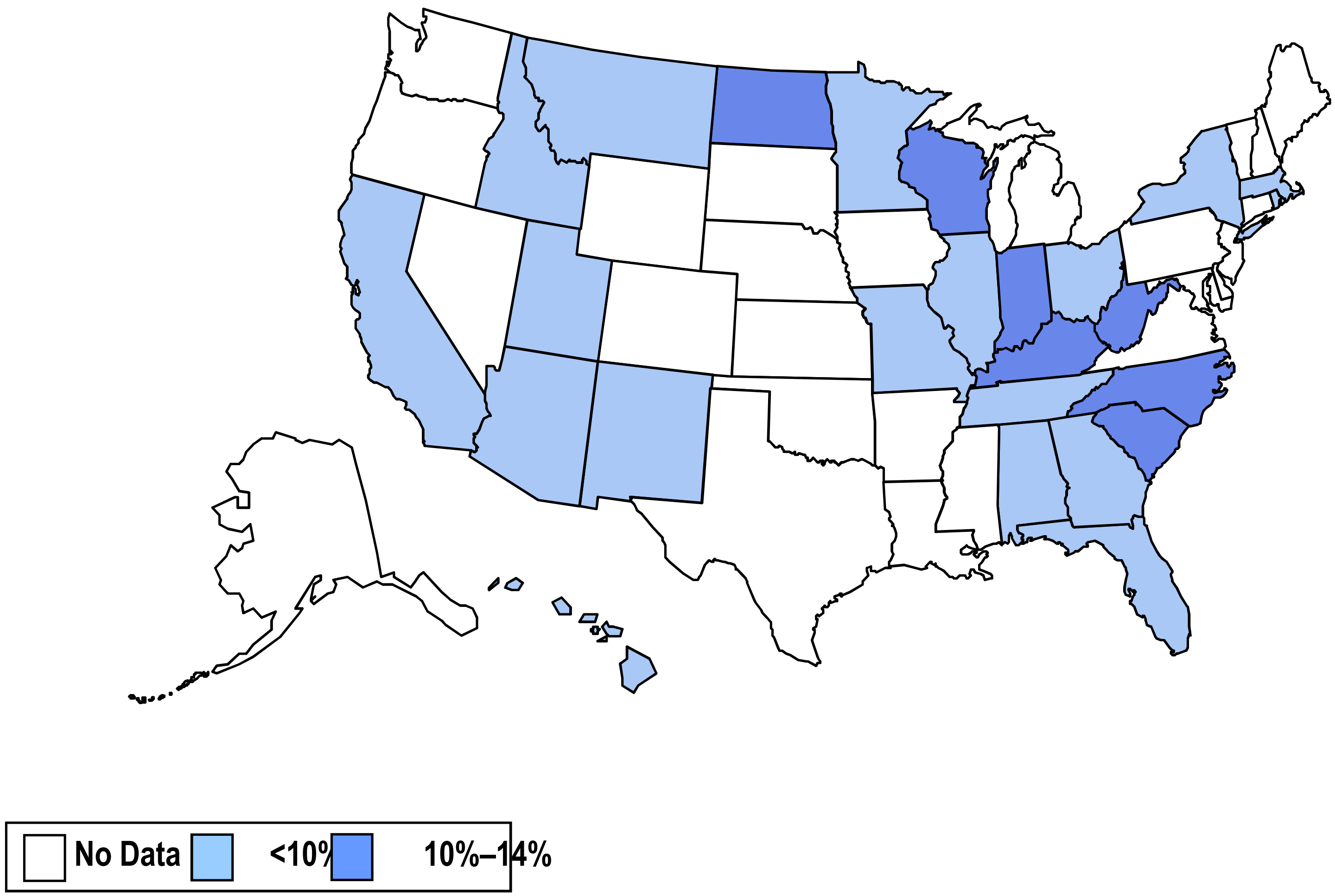
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 1986

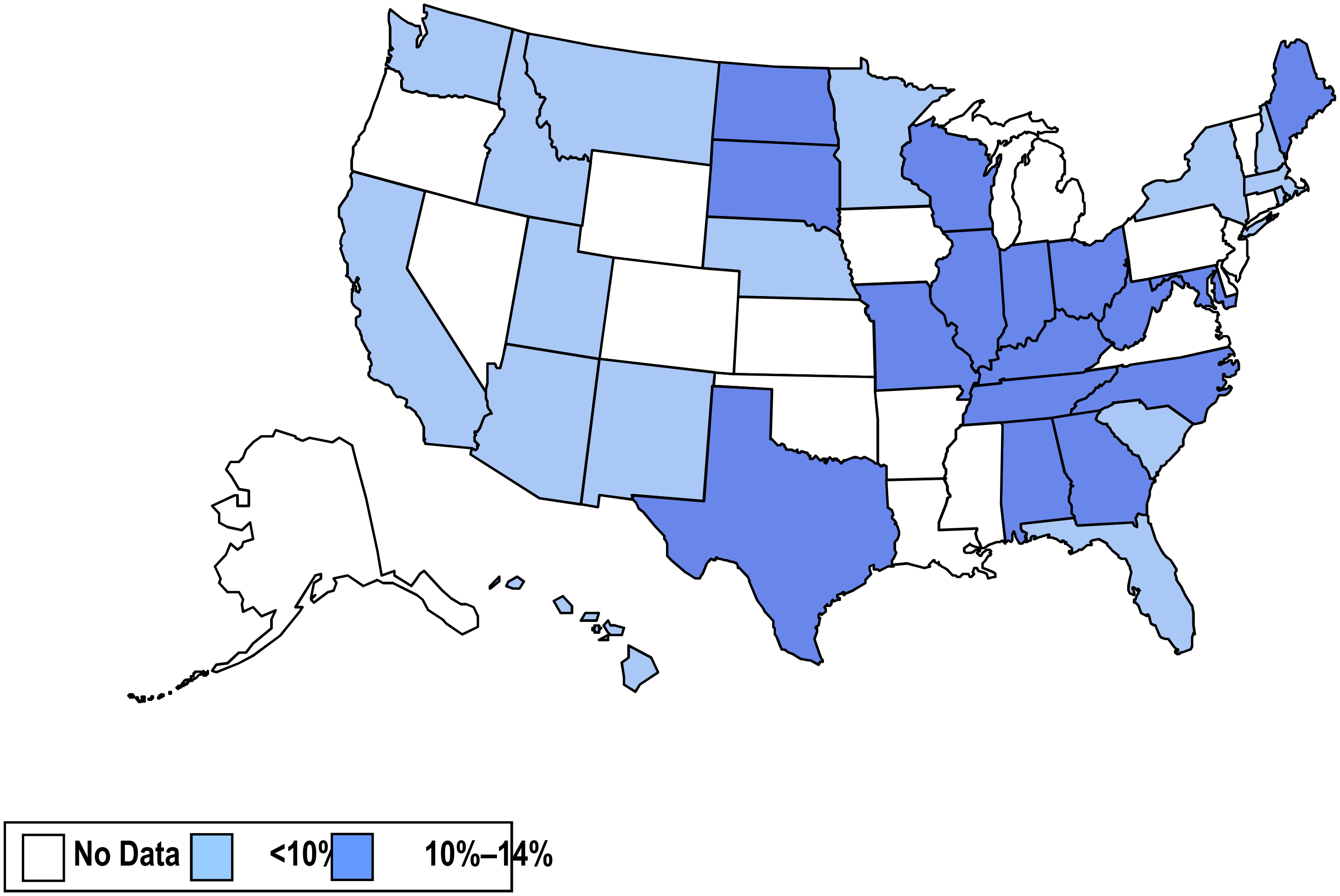
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 1987

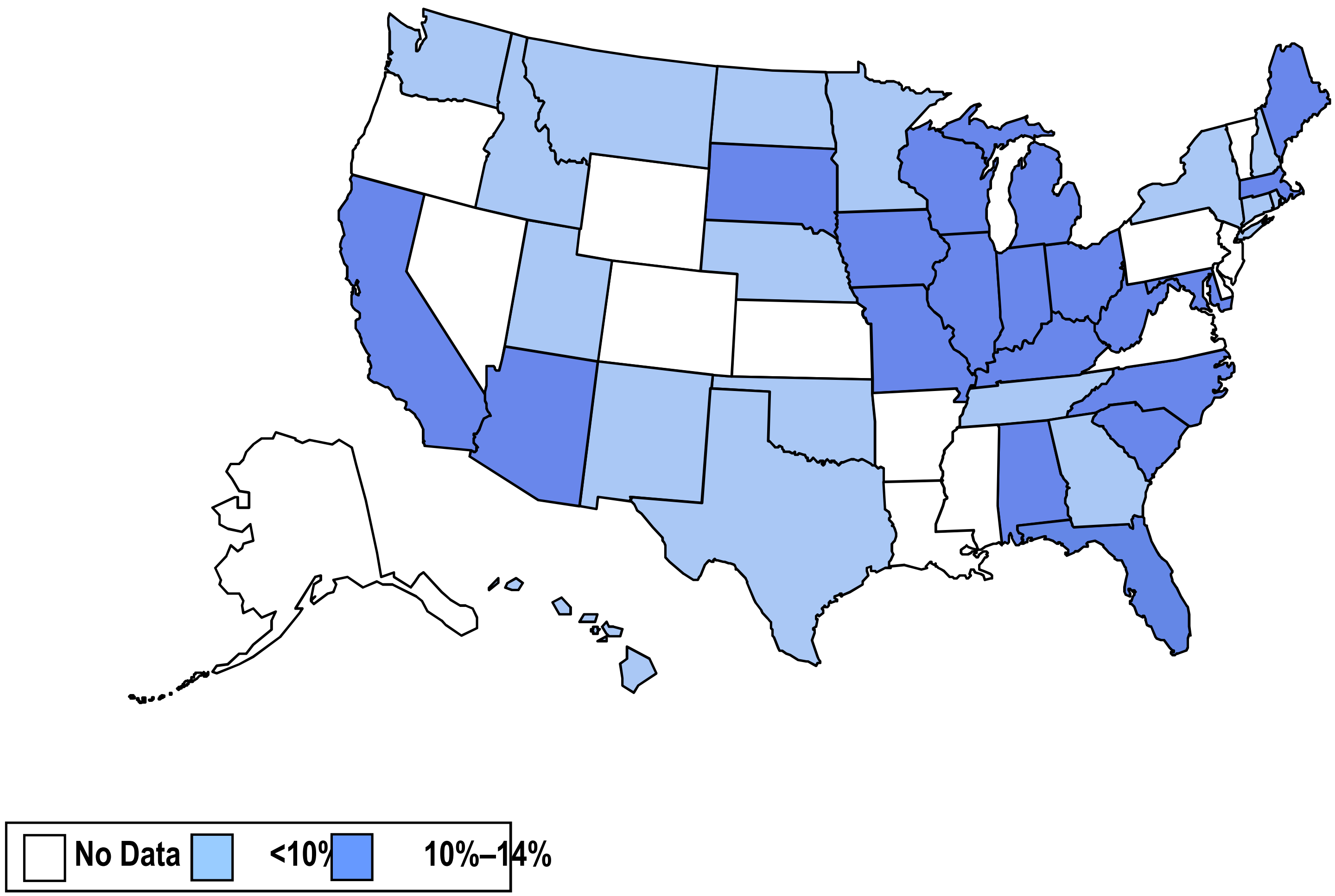
(*BMI ≥30, or ~ 30 lbs. overweight for 5’ 4” person)



Obesity Trends* Among U.S. Adults

BRFSS, 1988

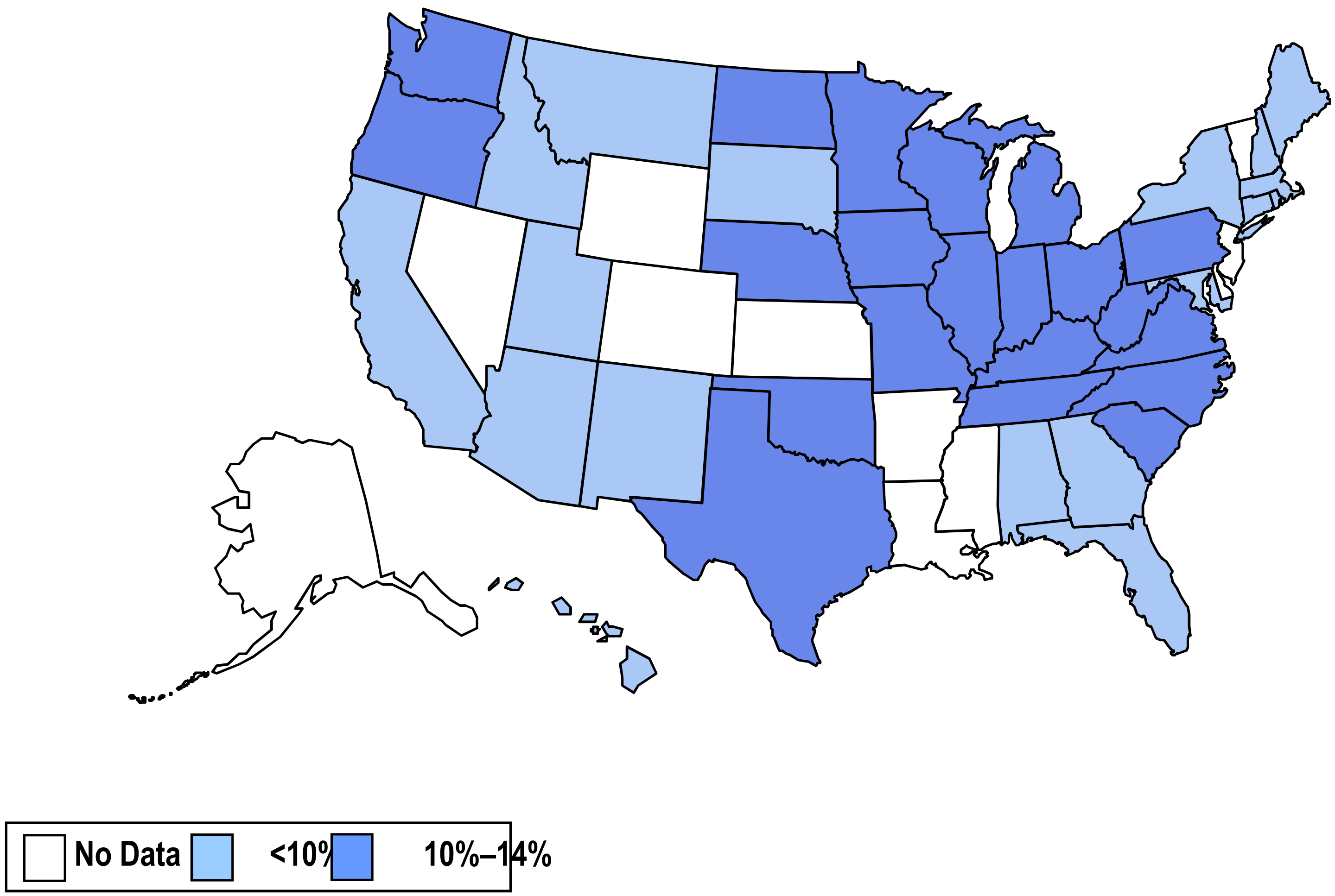
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 1989

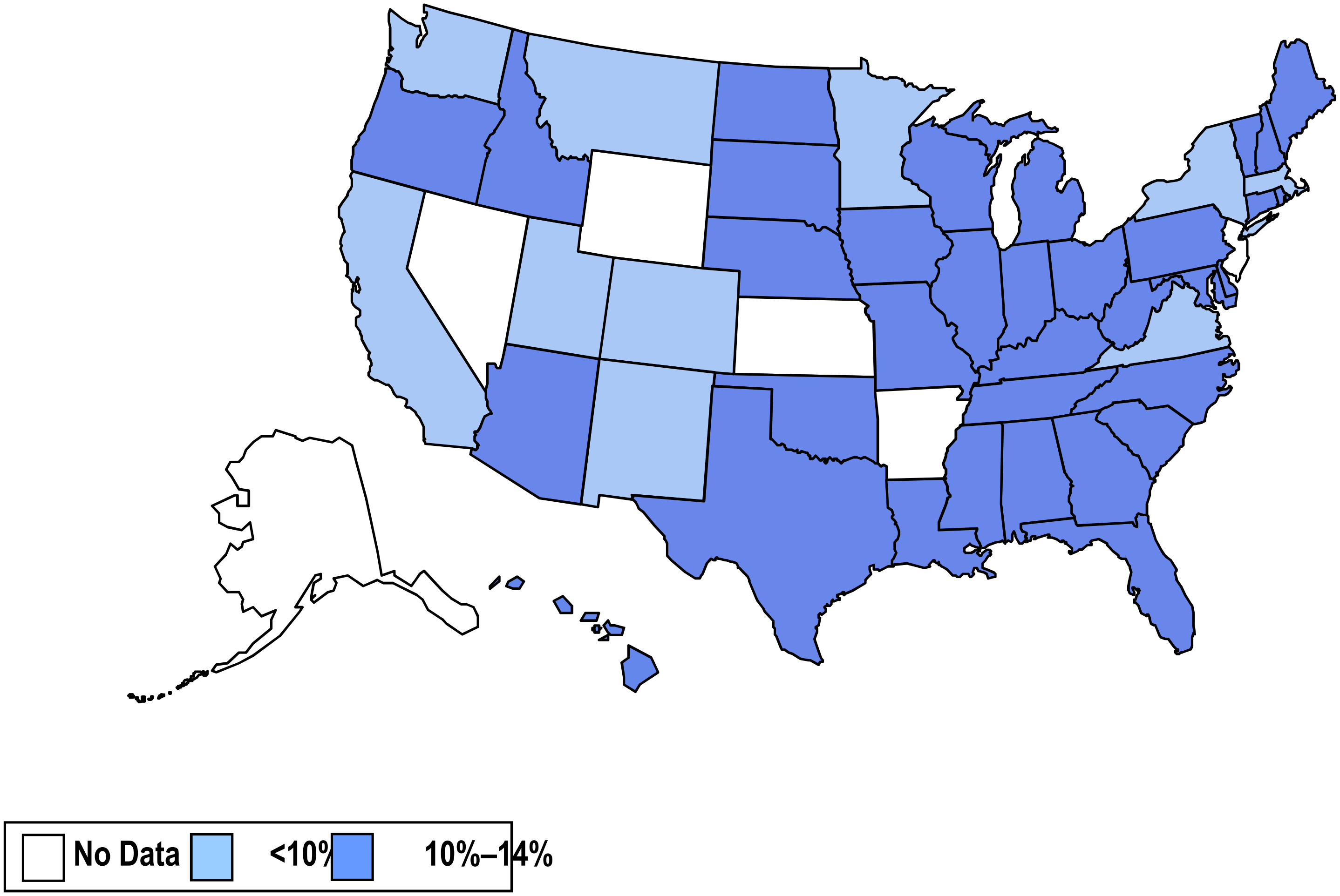
(*BMI ≥30, or ~ 30 lbs. overweight for 5' 4" person)



Obesity Trends* Among U.S. Adults

BRFSS, 1990

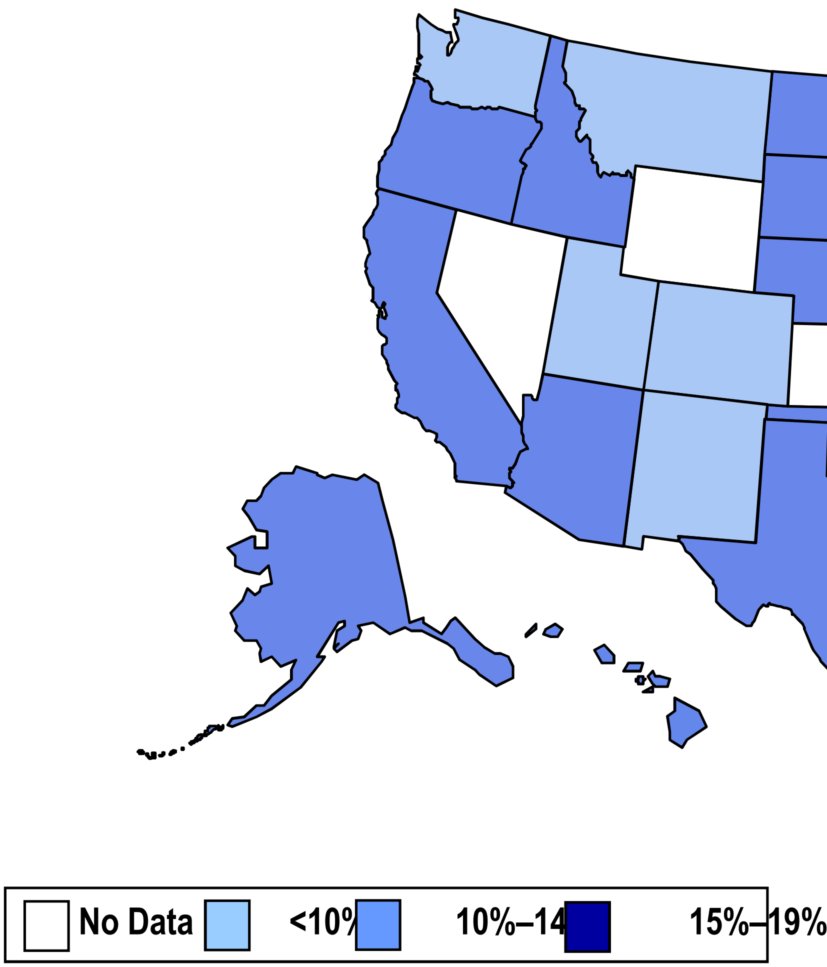
(*BMI ≥30, or ~ 30 lbs. overweight for 5' 4" person)



Obesity Trends* Among U.S. Adults

BRFSS, 1991

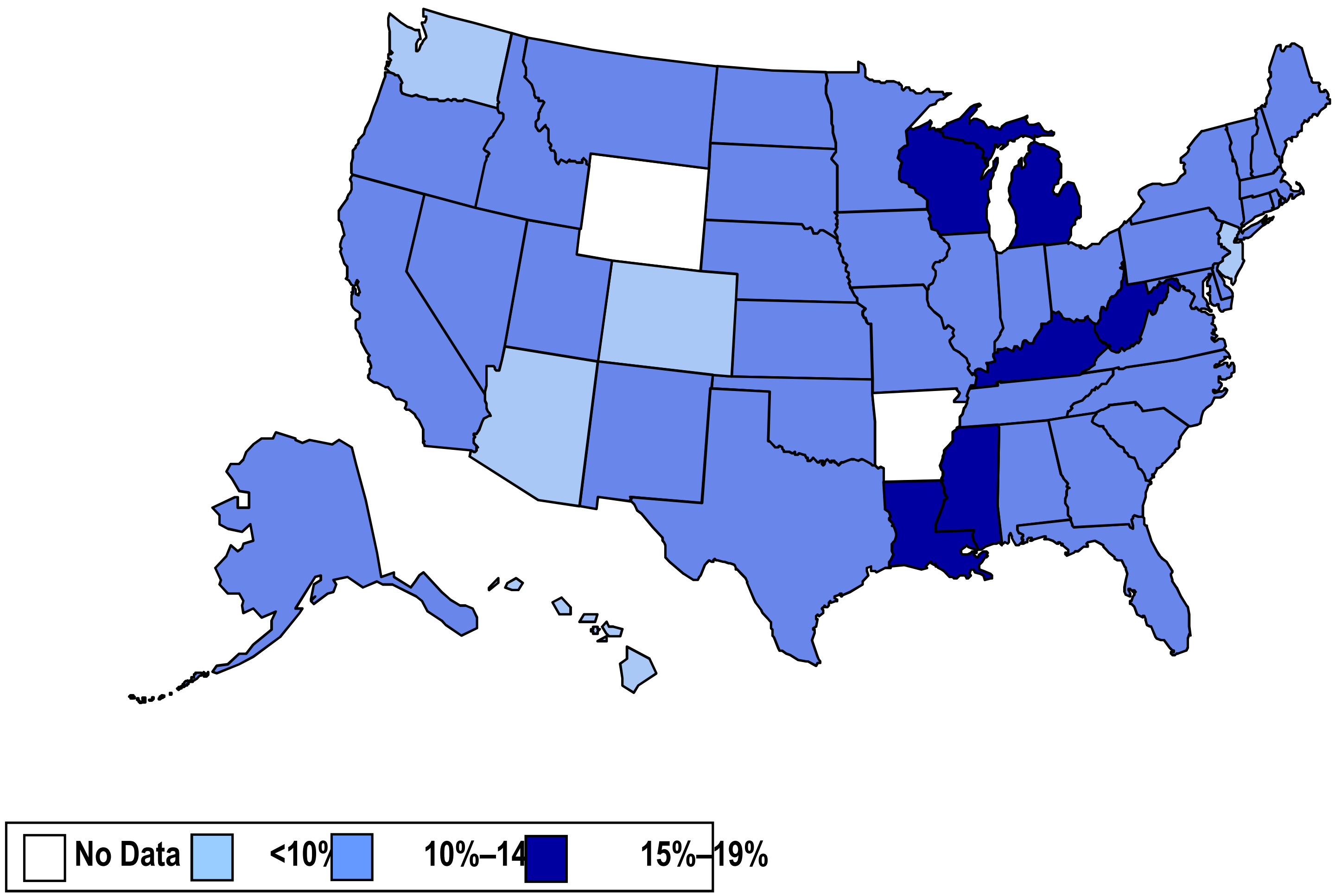
(*BMI ≥30, or ~ 30 lbs. overweight for 5' 4" person)



Obesity Trends* Among U.S. Adults

BRFSS, 1992

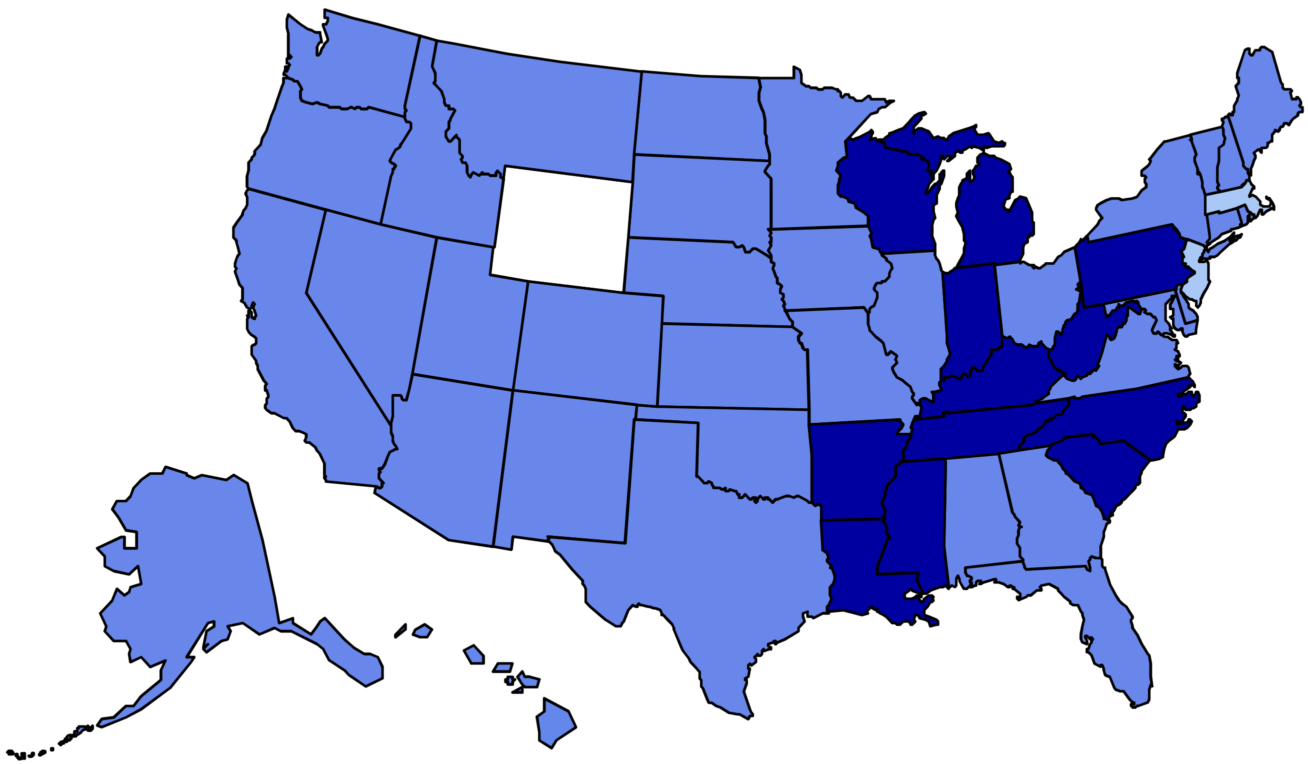
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 1993

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)

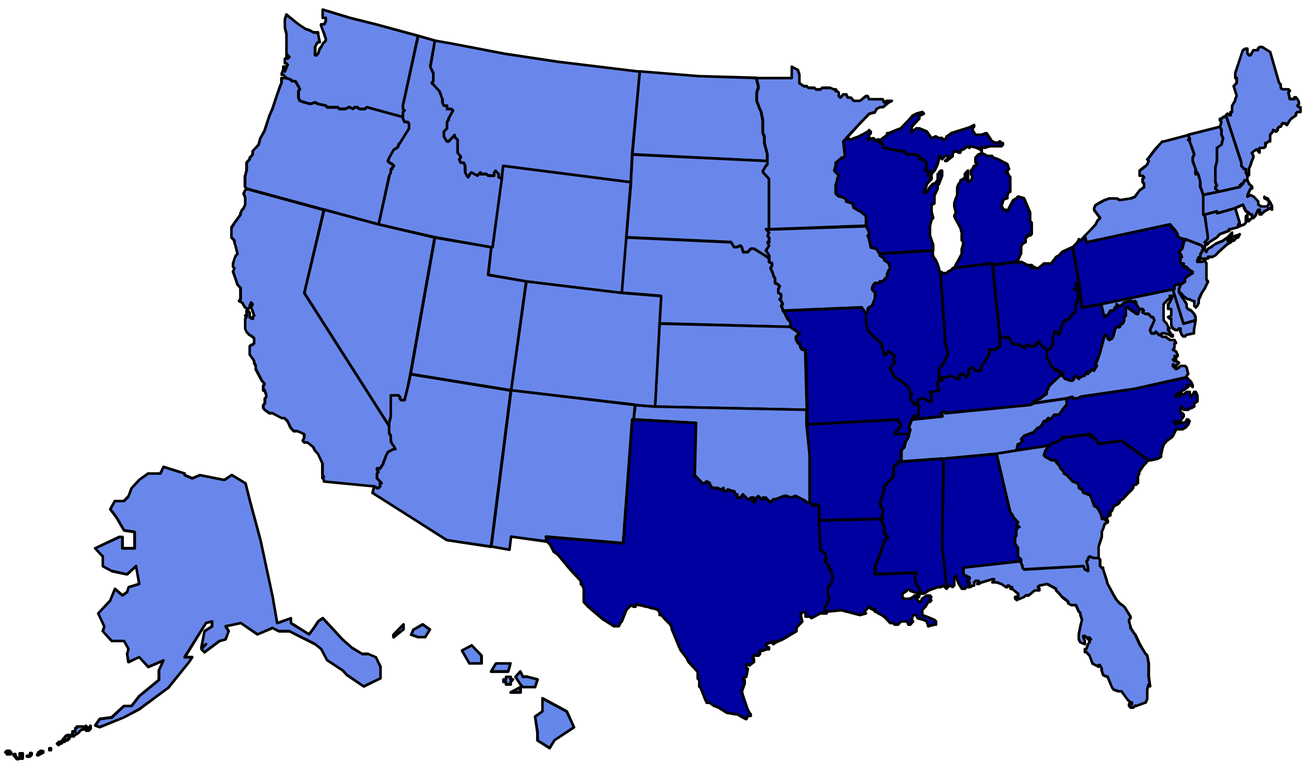


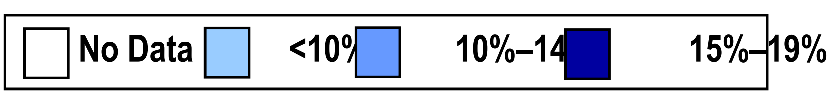
No Data | <10% | 10%–14 | 15%–19%

Obesity Trends* Among U.S. Adults

BRFSS, 1994

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)

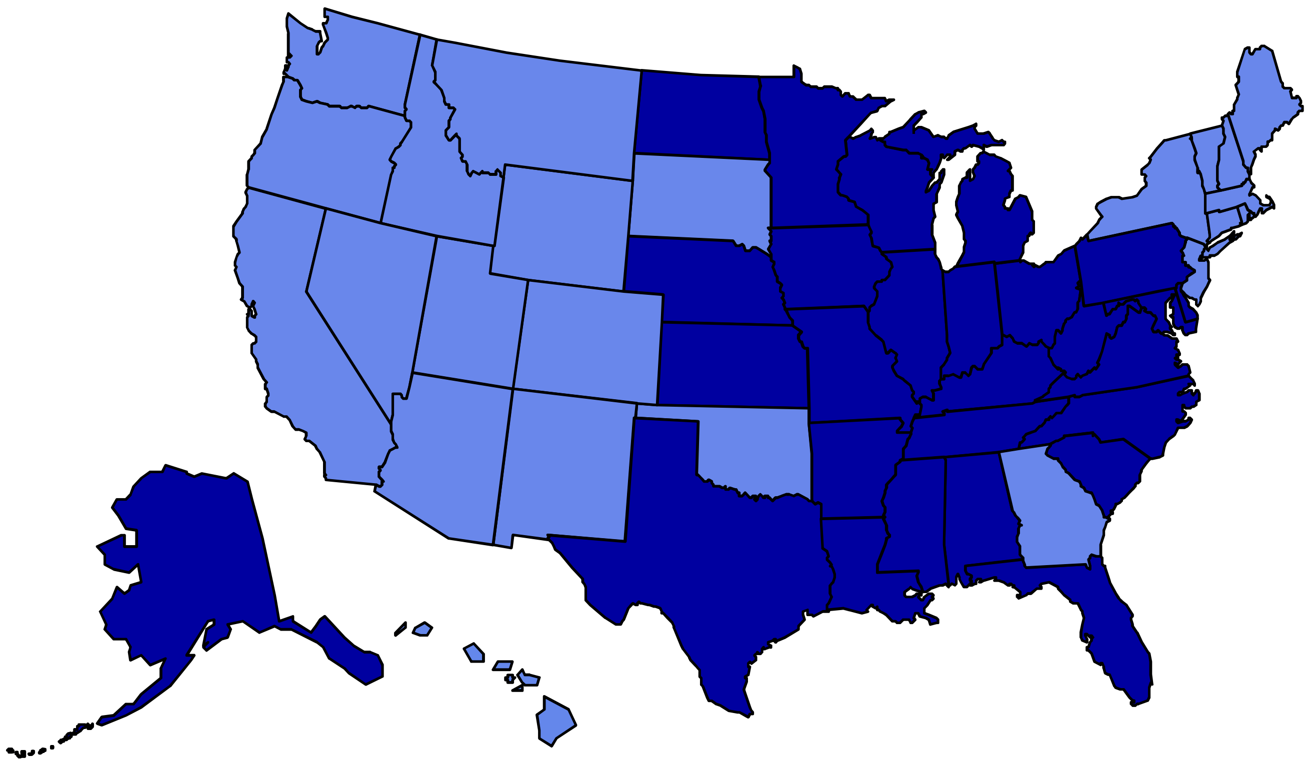


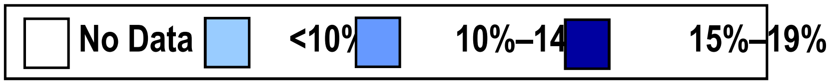


Obesity Trends* Among U.S. Adults

BRFSS, 1995

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)

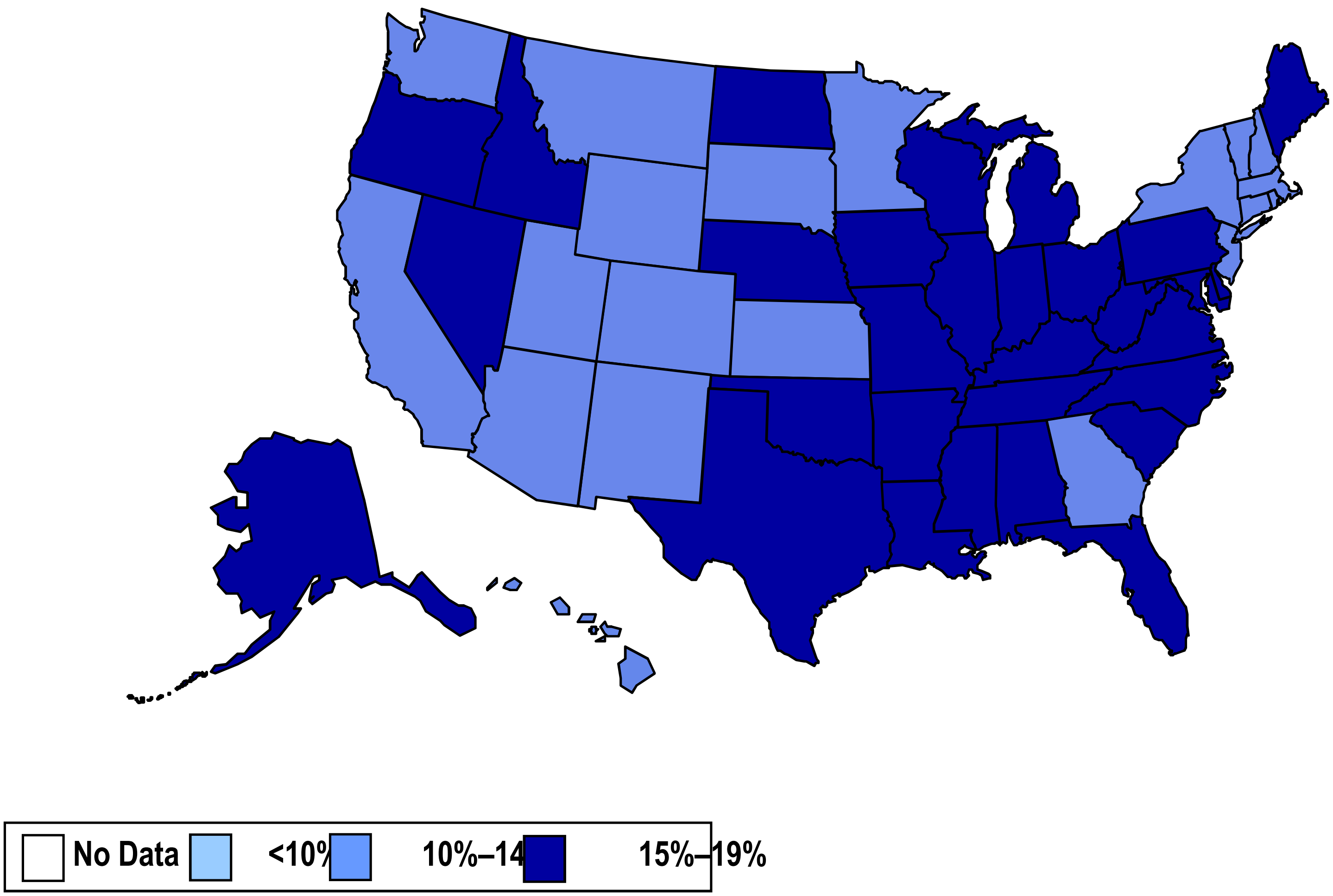




Obesity Trends* Among U.S. Adults

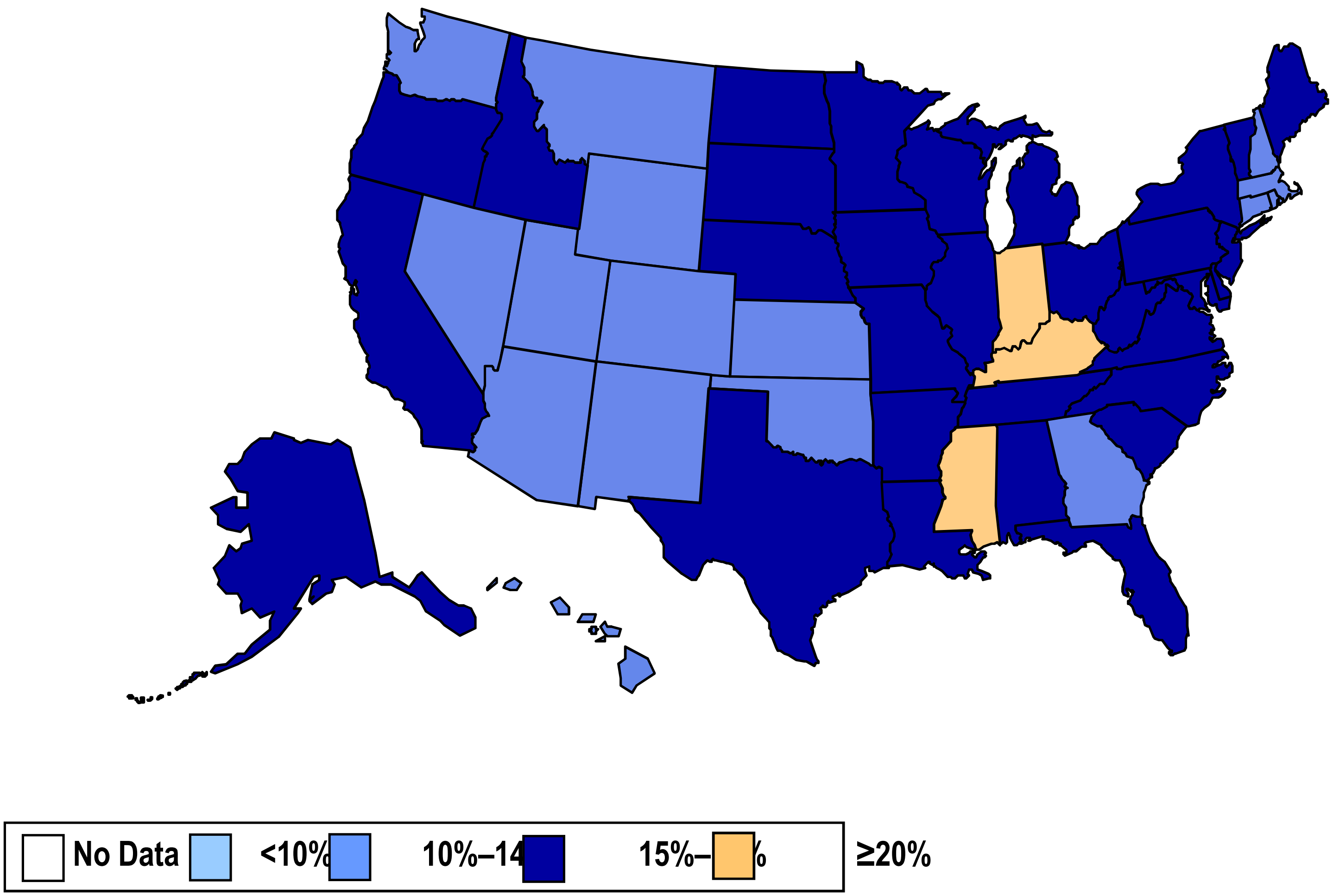
BRFSS, 1996

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults
BRFSS, 1997

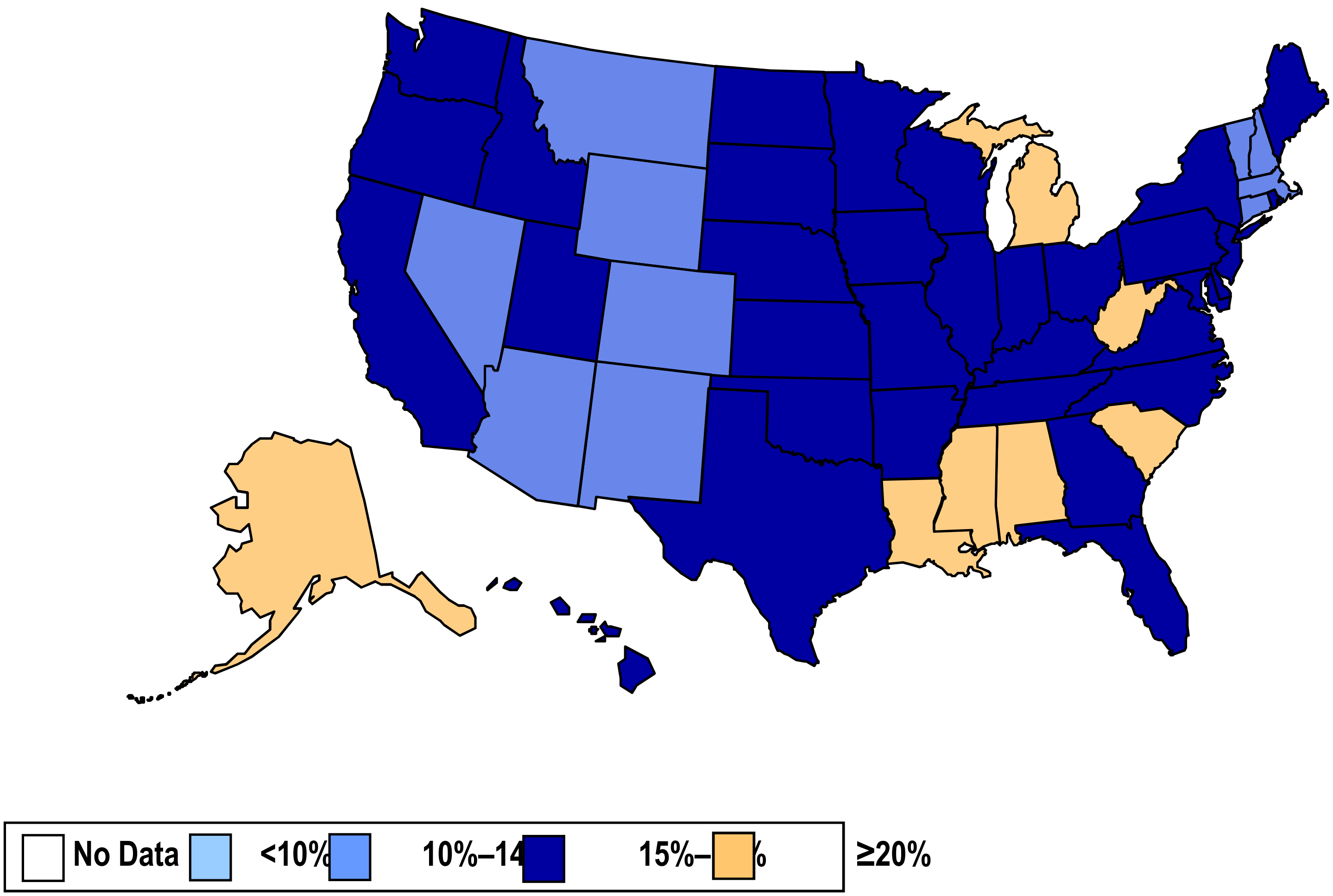
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

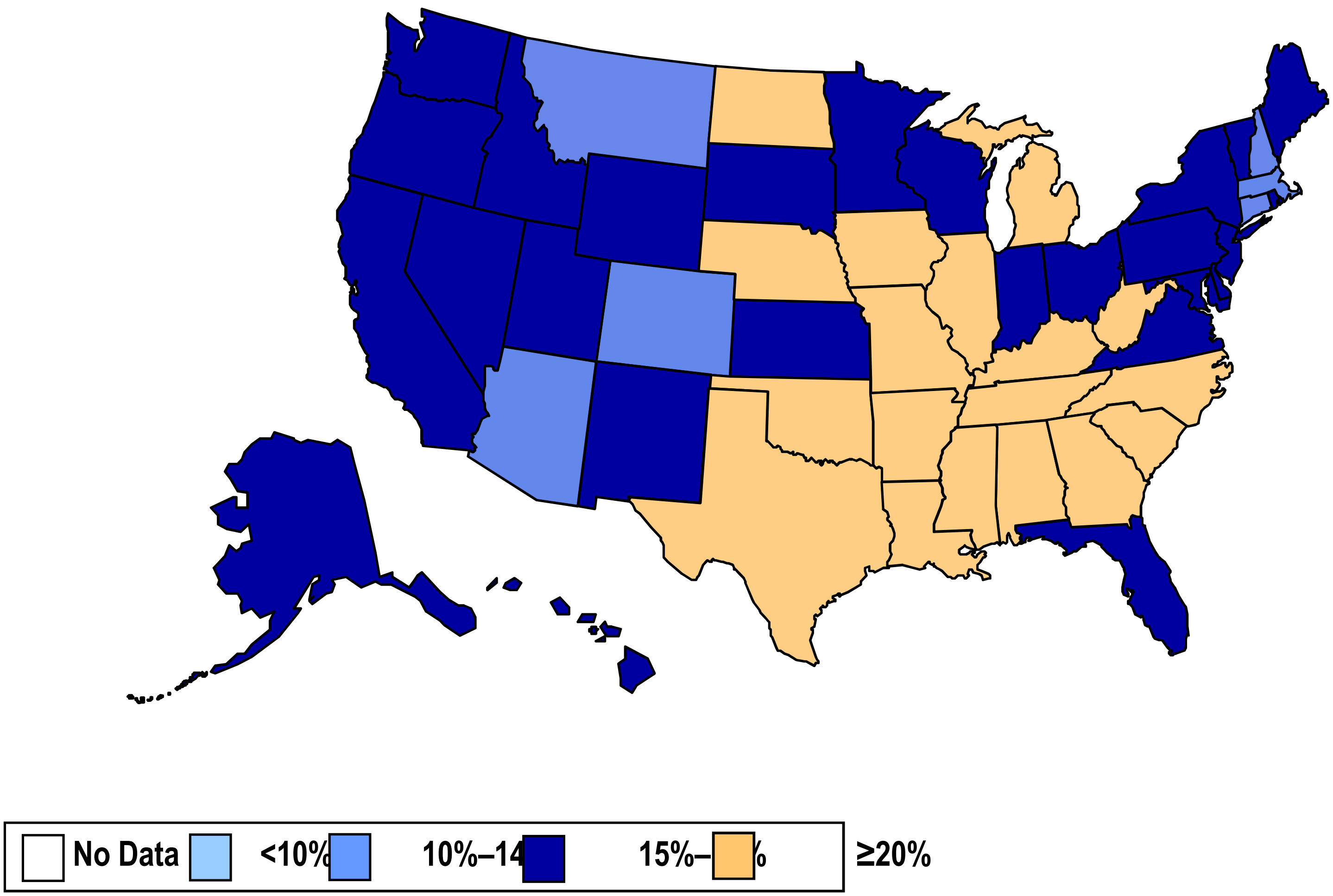
BRFSS, 1998

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults
BRFSS, 1999

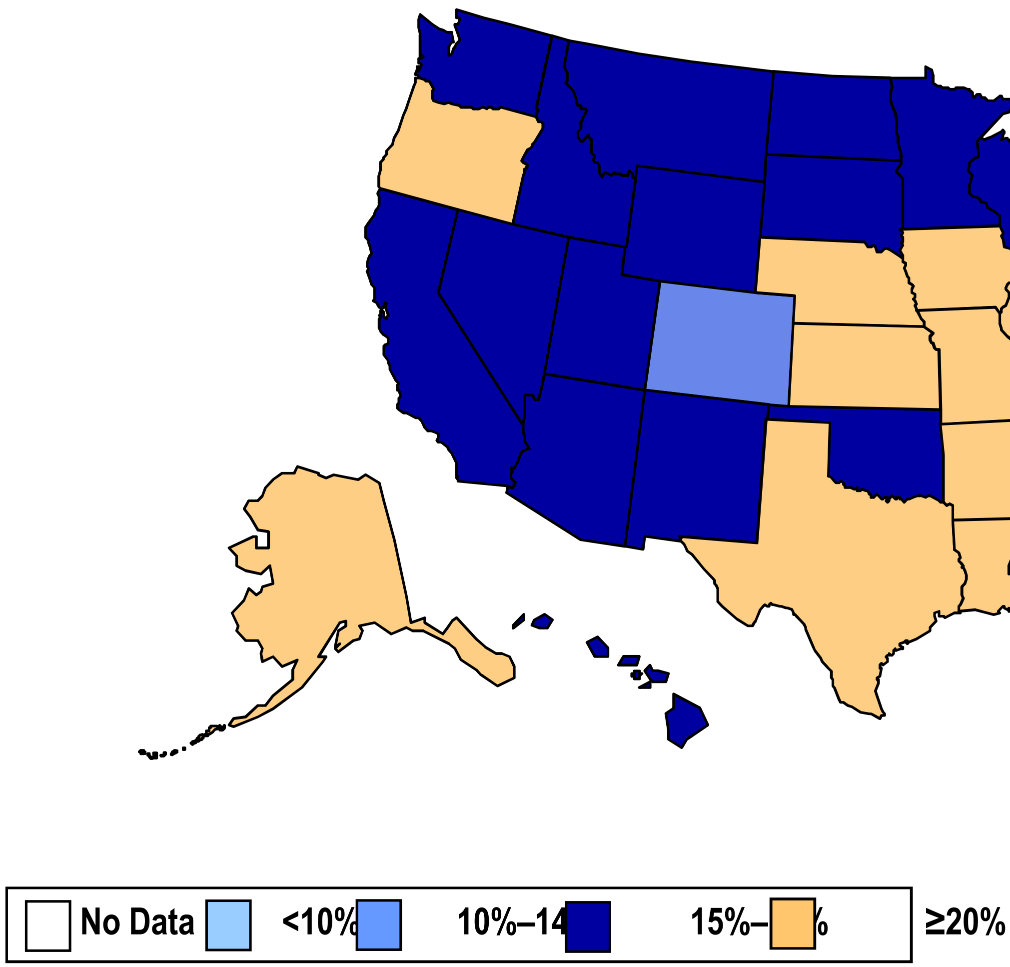
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 2000

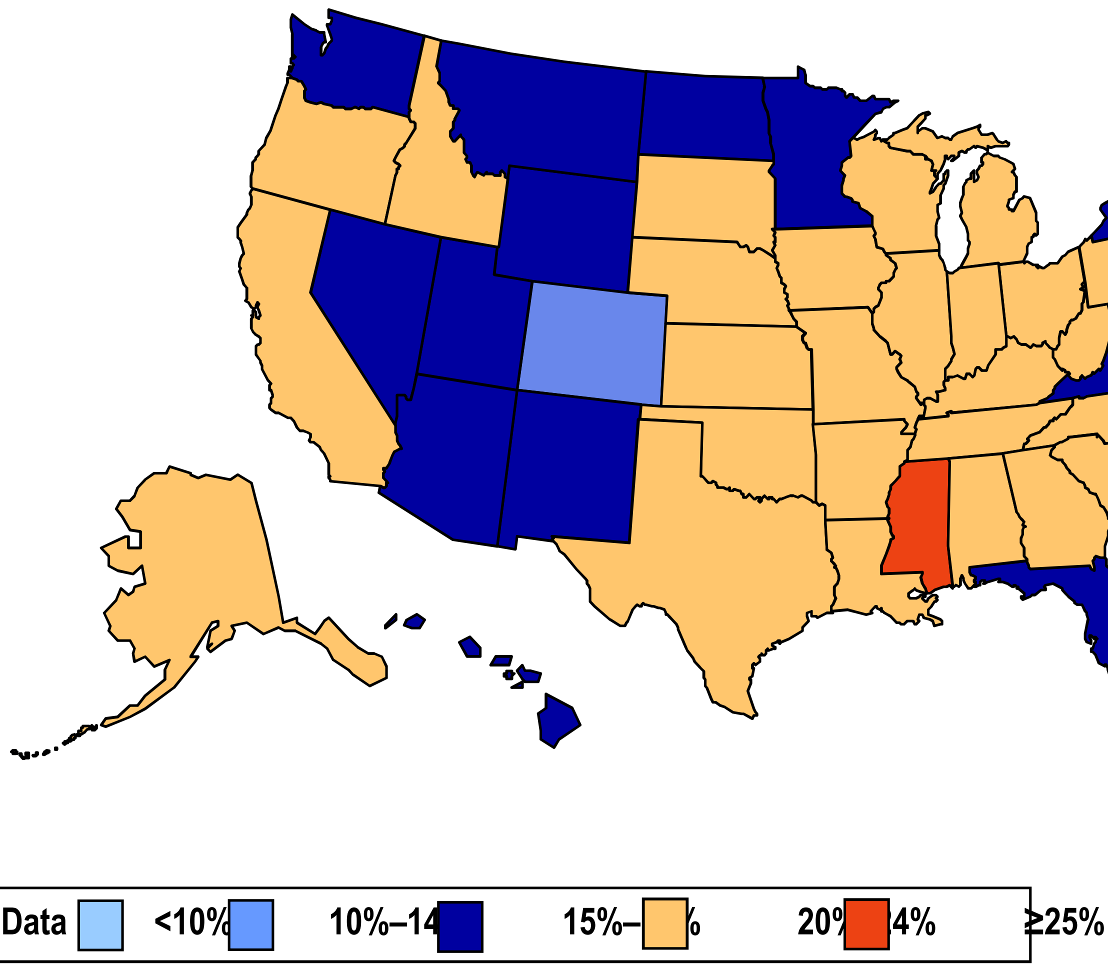
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 2001

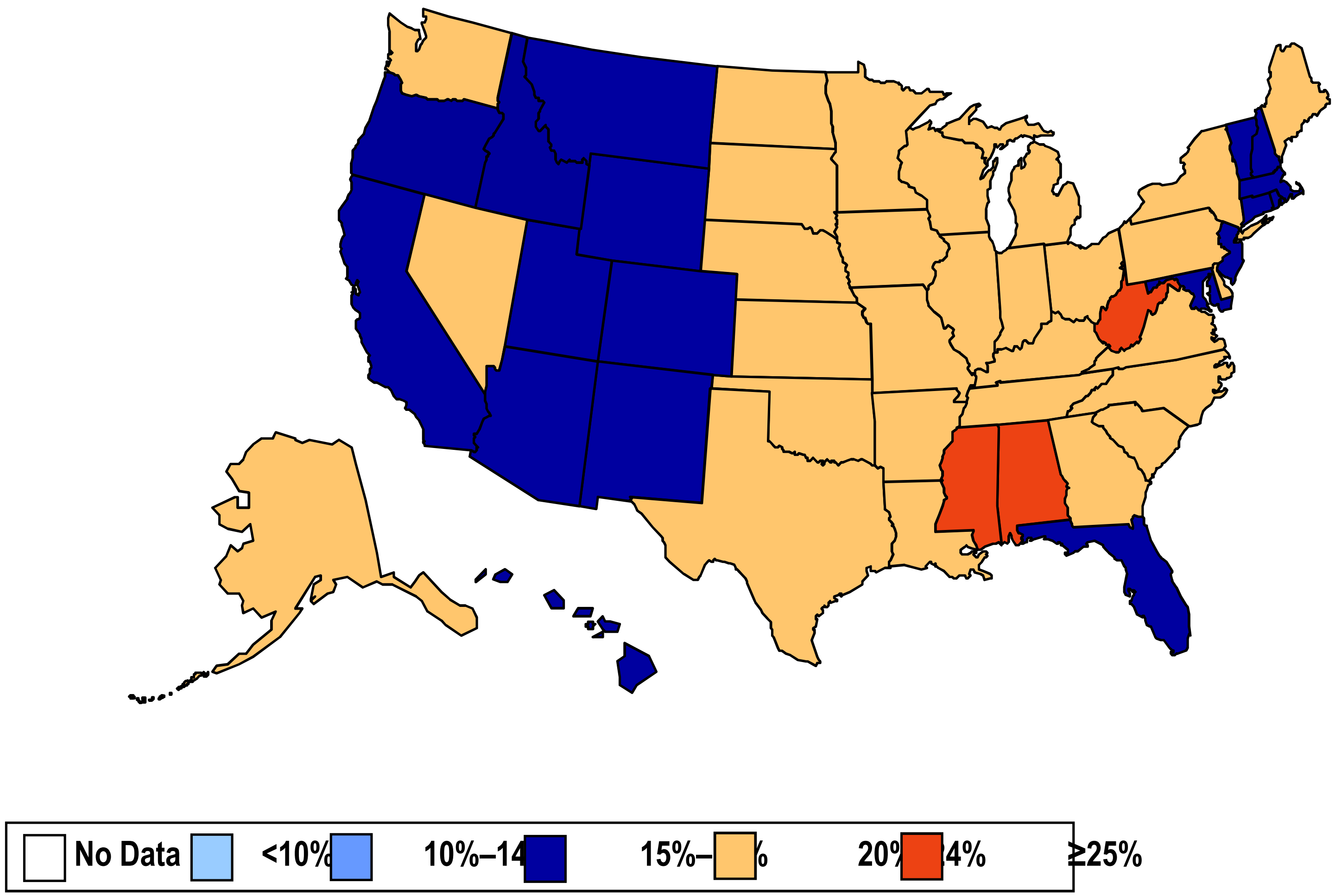
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

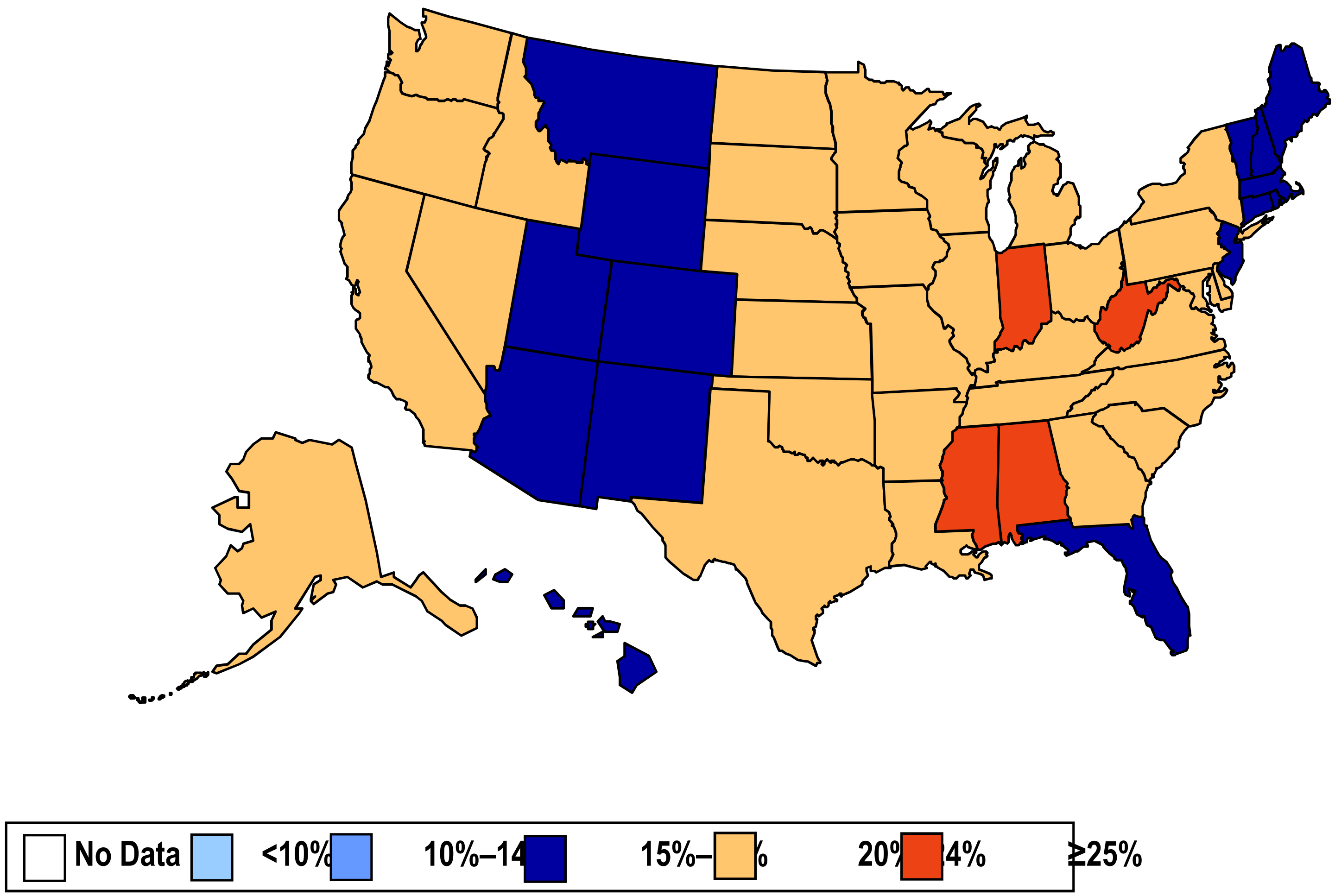
BRFSS, 2002

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults
BRFSS, 2003

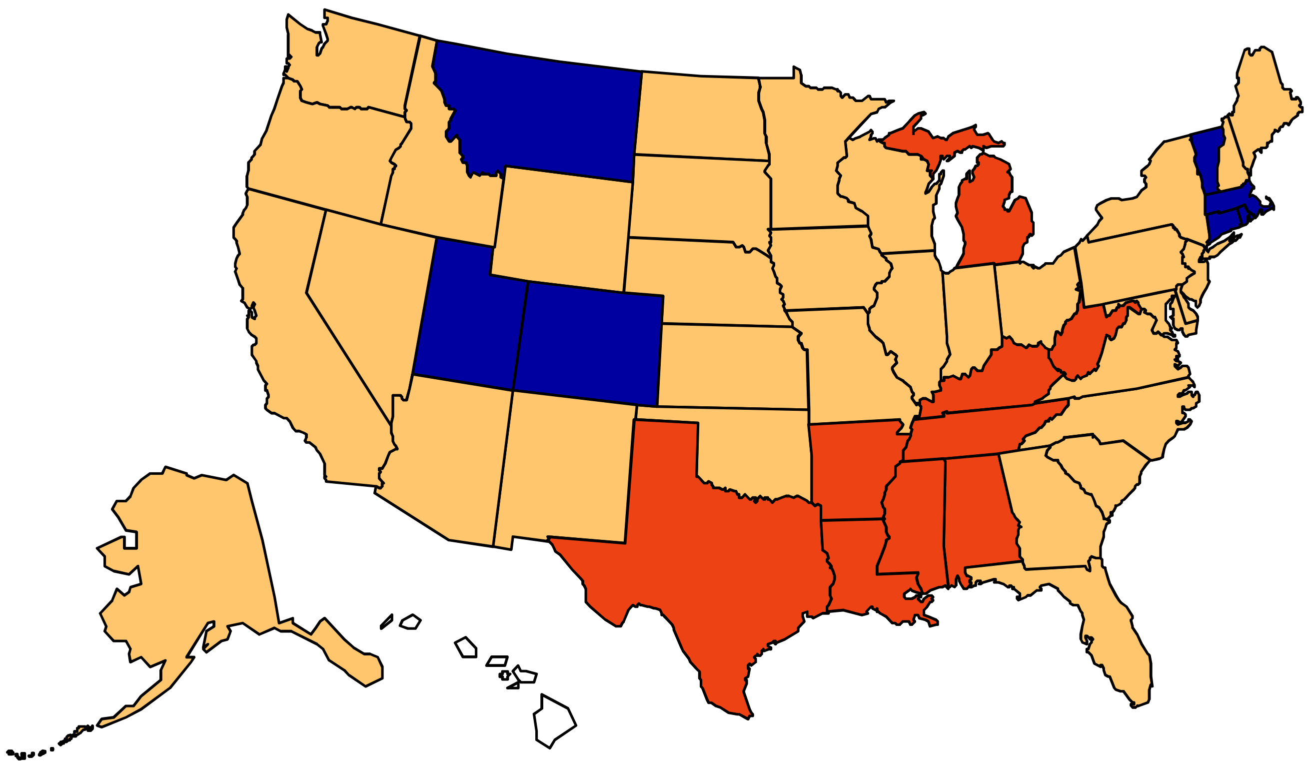
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 2004

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)

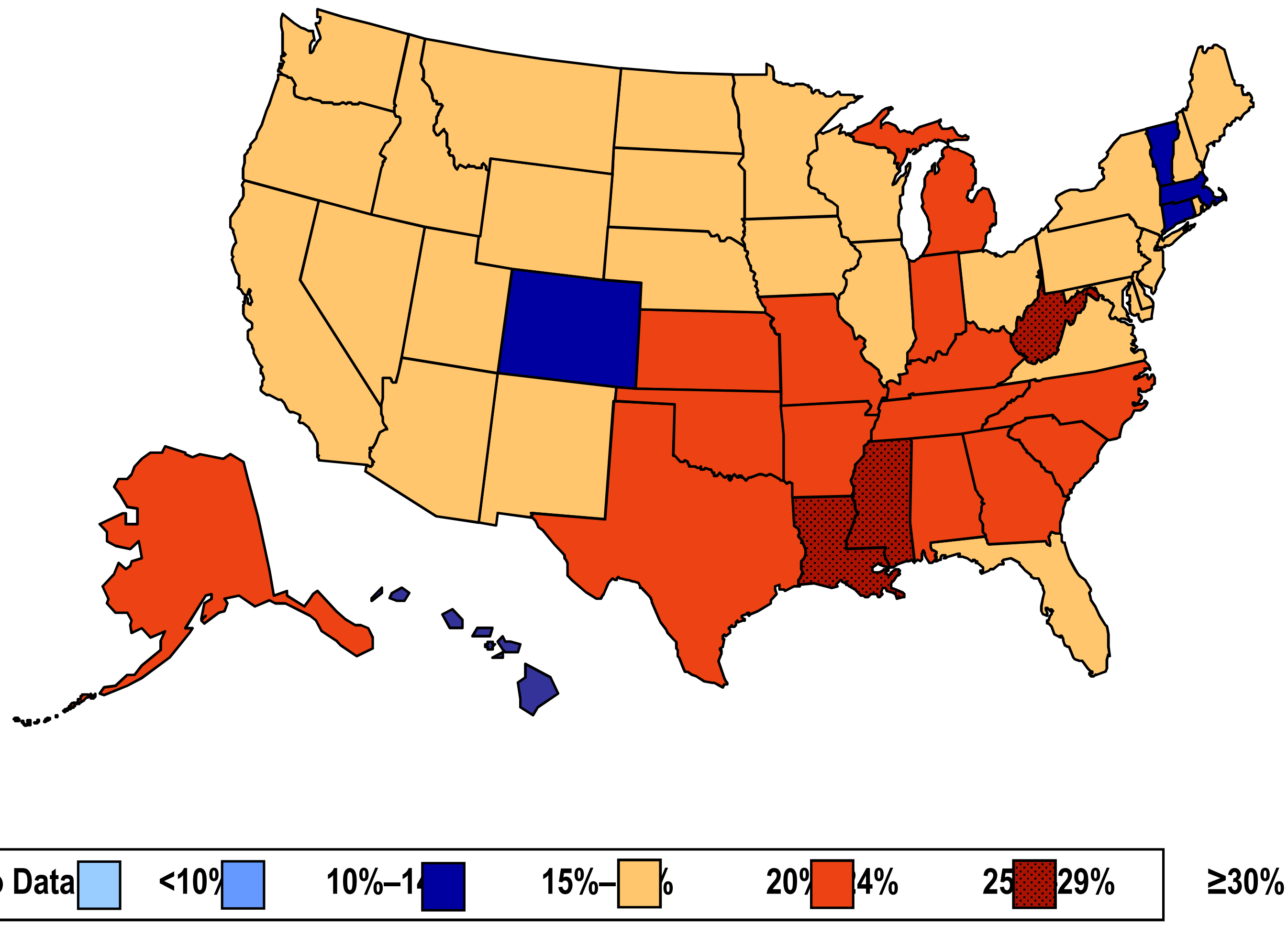


No Data **<10%** **10%–14** **15%–** **%** **20%** **4%** **≥25%**

Obesity Trends* Among U.S. Adults

BRFSS, 2005

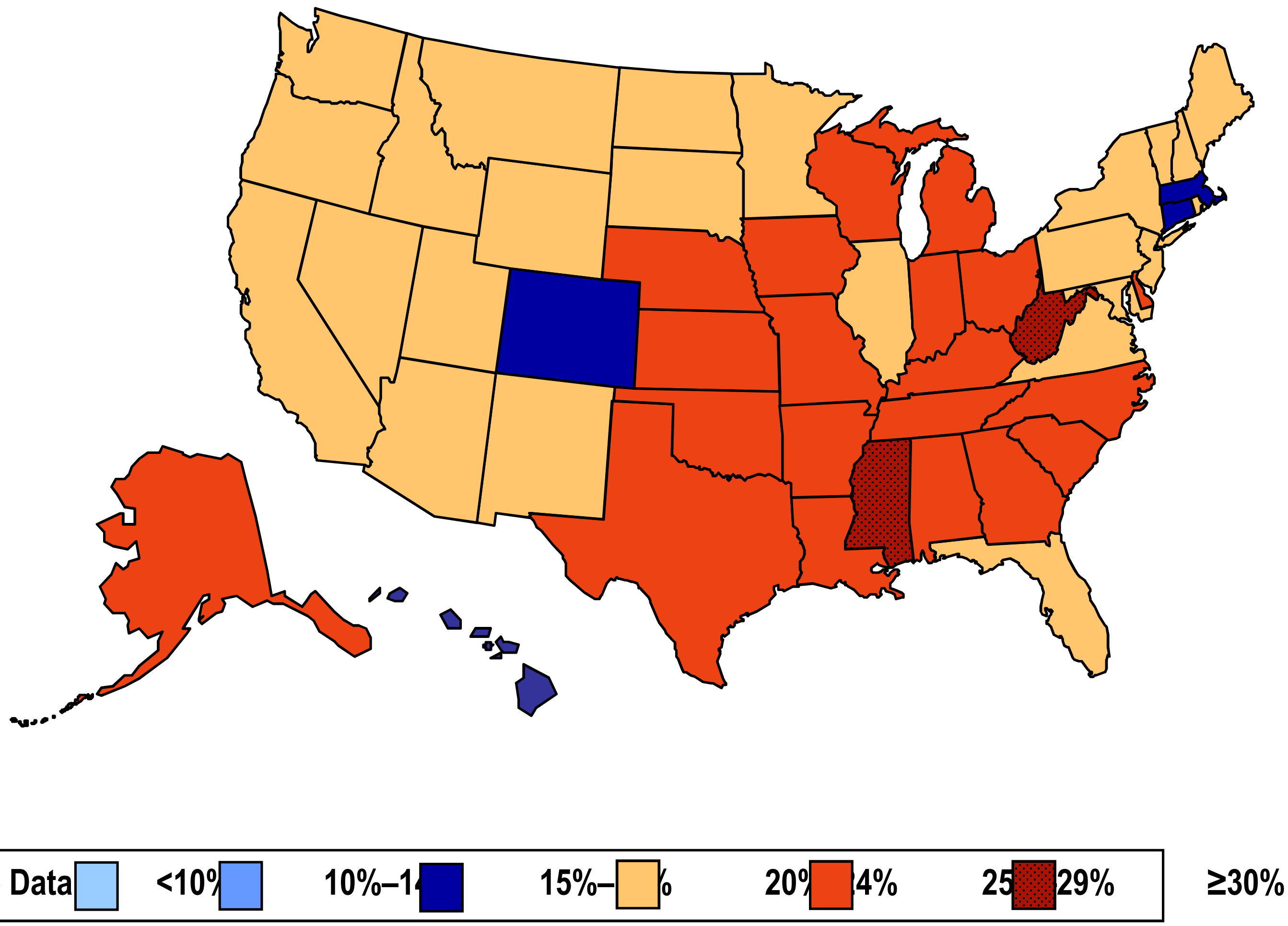
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 2006

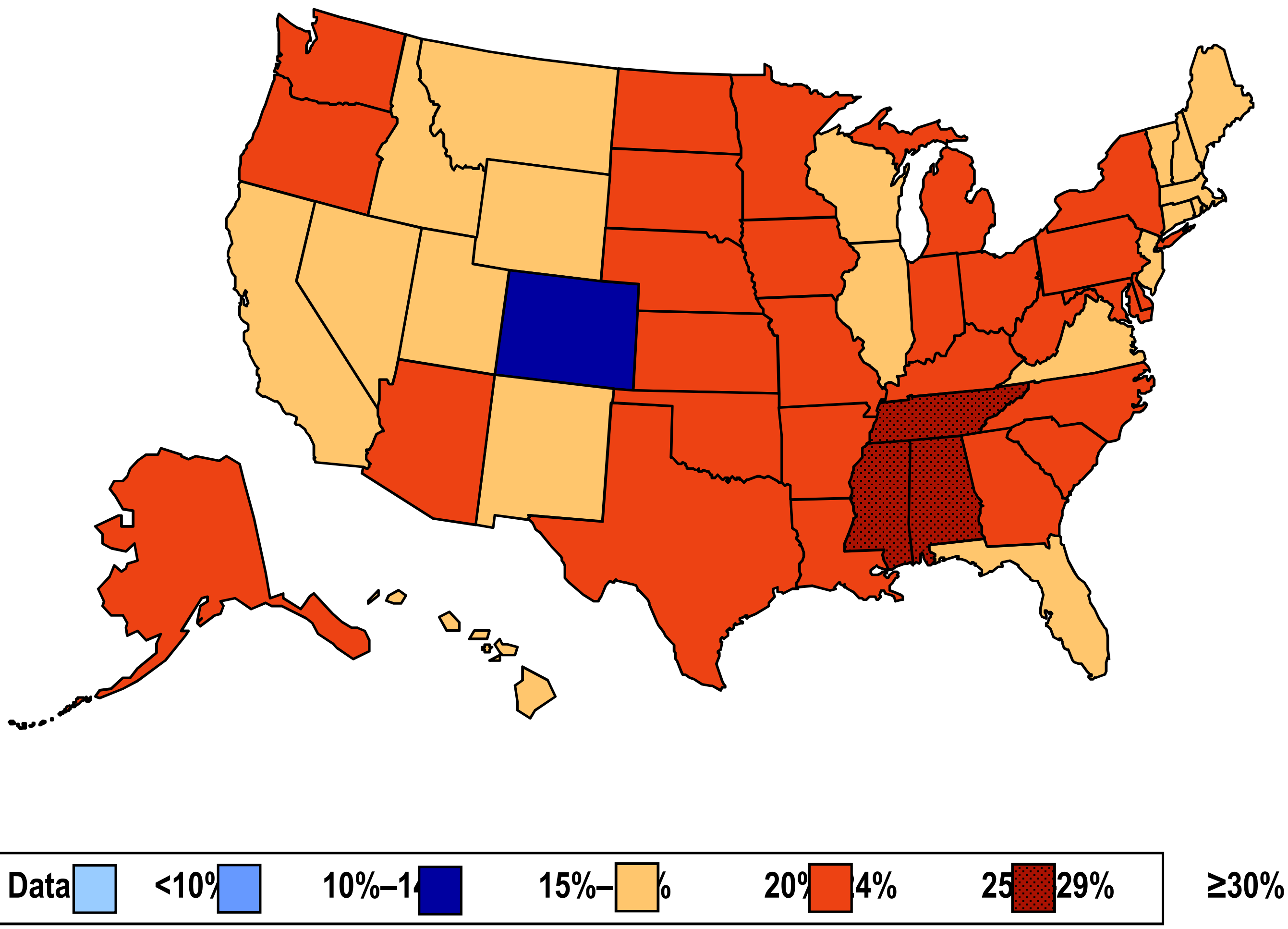
(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults

BRFSS, 2007

(*BMI ≥30, or ~ 30 lbs. overweight for 5′ 4″ person)



Obesity Trends* Among U.S. Adults
BRFSS, 1990, 1998, 2007
(*BMI ≥30, or about 30 lbs. overweight for 5’4” person)