

Natural inorganic (“not from living things”) pigments (Adapted from <http://www.handprint.com/HP/WCL/pigmt1a.htm>)

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Natural inorganic pigments are among the oldest used by humans. They first appear in the funeral preparation of human remains from 60,000 years ago, and in multi-colored (“polychrome”) cave art from about 20,000 years ago. Mined in prehistory from surface deposits of clay and rock, many inorganic pigments have shown extraordinary permanence over long periods of time.

With few exceptions, inorganic pigments are combinations of a mineral element with oxygen and other elements (most often sulfur, silicon or carbon) that fall in the chemical classes known as oxides, oxide hydroxides, sulfides, sulfates, silicates and carbonates.

The pigments in this category that have been of importance to watercolor painting include:

Red earths. A large and diverse category of pigments, all made from earths (mostly clays) containing large proportions of iron oxide (the dark violet to light red hematite or everyday rust, the orange to yellow lepidocrocite, or the dark brown maghemite) that is processed and sold as natural iron oxide. The pigment color may range from a dull yellow through a dull deep yellow, dull orange, dull red or dark brown to near black. The color depends on the average particle size, the presence of manganese or other elements (which darkens and dulls the color), and whether water is chemically bonded within the iron oxide crystals. (The dull red orange to yellow hydrous oxides contain water, the maroon to dull red anhydrous oxides do not.) Although red iron oxides occur in all parts of the world and have been used as pigments since antiquity, rich deposits are currently found near Malaga, Spain (Spanish red, which has a characteristic brownish undertone) and in Ormuz, in the Persian Gulf (Persian red). Historically, European sources of yellow brown earths were mined near Leghorn or Siena (in Tuscany, Italy); these are the siennas, containing roughly 50% iron oxide and less than 1% manganese dioxide. The dark red or brown earths or umbers, containing 45%-70% iron oxide and 5% to

20% manganese dioxide, were originally imported to Europe from Turkey (via Venice), but are now mined primarily in Cyprus. The name probably derives not from the Italian region of Umbria but from the Latin *ombra* or shadow, referring to the original use of dark iron oxides as shadow colors. These earths are often “burned” (calcinated or roasted at a dull red heat) to darken them (burnt sienna, burnt umber), a technique that was probably suggested around 2000 BCE by the visible reddening or darkening of pottery after it had been fired or glazed. Natural manganese ores have sometimes been added to red earths create darker red, violet or black colors in pottery clays or glazes. Due to growing scarcity of high quality natural deposits of iron oxides, most artists’ colors are now made from synthetic iron oxides.

Yellow earths. Natural earths containing silica and clay, hydrous forms of iron oxide (yellow brown limonite or the brown yellow to green yellow goethite), and traces of gypsum or manganese carbonate. Like the red iron oxides they are found around the world and have been used as pigments since prehistory. French ochre, historically one of the best grades of limonite, contains about 20% iron oxide and is high in silica. Currently workable deposits for yellow oxides are located in the Republic of South Africa and France. Most often sold as yellow ochre or brown ochre. Most yellow clays are normally not “burnt” as heat does relatively little to alter their color.

Green earths. Clays containing large amounts of silica and the green minerals glauconite and celadonite, consisting essentially of hydrous iron, magnesium, and aluminum potassium silicates. Color varies from a dark, grayish blue green to a dark, dull yellowish green. Completely lightfast and chemically inert, green earth or *terre verte* has been used around the world since ancient times. In Europe, the first documented use in paintings is in Roman frescos; it was also commonly used in the Middle Ages as an underpainting for flesh tones and shadows. Originally extracted from deposits in central Europe--today’s Czech Republic, near Verona

in Italy, or in France--modern supplies come from high quality deposits in Cyprus. Most of these pigment deposits originated as marine clays. In watercolors the typical color is light valued (diluted), and paints made from the genuine pigment tend to be thin and gummy. The label *terre verte* is often applied to paints mixed from other inorganic pigments, typically chromium oxide green or viridian mixed with a red iron oxide.

Lapis lazuli. A complex rock mixture of the deep blue mineral lazurite (natural ultramarine, chemically the most complex mineral pigment) with calcite or calcspar and iron pyrite. The name ultramarine comes from *azzurro oltramarino* ("blue from over the sea"), the name used to distinguish it from *azzurro della magna* (mountain blue, azurite). Lapis is found in China, Tibet and Central Asia, and used in jewelry, sculpture and painting in ancient Babylonian and Egyptian cultures. It was imported to Europe by way of Venice, ground to a powder and separated from impurities for use as a very costly reddish blue pigment in medieval manuscripts and art. The color is decomposed by acids but is otherwise very permanent. Simple grinding and washing produces a disappointing, pale grayish blue powder (called ultramarine ash) to get a saturated color, the pure pigment must be extracted by mixing the ground mineral with melted beeswax, resins or oils, wrapping the hot bolus in cloth, and kneading in a hot dilute solution of lye, a method used since the 13th century. Modern synthetic ultramarine blue closely matches the best preserved examples of lapis lazuli pigment in old paintings but is slightly darker and redder.

Azurite. The less common greenish blue crystals of copper carbonate, called "mountain blue" (Bergblau) in Germany, which occurs in copper ore deposits around the world. Azurite has been used as a pigment since antiquity, but was often displaced by other synthetic pigments (such as Egyptian blue, copper calcium silicate), or

used as an underpainting to the more expensive ultramarine. The crystals are usually coarsely ground to the texture of fine sand because the color shifts from deep blue to a weak, pale blue as particle size decreases. Azurite is decomposed by acids and is blackened by heat and some oil vehicles and varnishes. An important pigment in Europe from the 15th to 17th centuries, it fell out of use when Hungary, the primary source of the natural pigment, was conquered by the Turks. Synthetic azurite was used in modern times primarily in housepaints; artists' colors relied almost exclusively on iron blue (Prussian blue) after the mid 18th century.

Malachite. The more common (green) form of hydrous copper carbonate, called mountain green, mineral green or *verdeazzurro* ("green azure"), found around the world in surface deposits of copper. The ancient Egyptians ground it to a powder for use as a green pigment; since Roman times the brighter synthetic copper pigments have usually been preferred for artistic uses. Used in European tempera and oil paintings from the 15th to 17th centuries; it fell out of use entirely by the end of the 18th century. The color significantly lightens and shifts toward blue as particle size decreases, and it is not permanent.

The main caution with natural inorganic pigments is that any paint containing them (in particular the siennas, umbers and ochres) will vary considerably across manufacturers (mineral impurities can noticeably affect the color).

Many of the traditionally natural inorganic colors — in particular the traditional earth colors (yellow ochre, raw sienna, burnt sienna, raw umber, burnt umber, and venetian or indian red) are no longer made with natural pigments. Significant differences can exist among earth pigment paints with exactly the same common name.