China's Ancient Gold Drugs

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Received: 20 April 2000

The earliest application of gold as a therapeutic agent was in China, and it was widely used by physicians and surgeons. For example, pure gold was used to treat furuncles, smallpox and skin ulcers and to remove mercury from skin and flesh; some ancient references noted that gold drugs can cure joint disease and disease in lungs. There were also prescriptions containing gold for curing measles and other diseases. Plant and animal medicines were used in ancient prescriptions and many of these contain gold as a trace element. Ancient China had remarkable achievements in the pharmacology of gold. The evolution of "medicinal gold" and "potable gold" also promoted the development of preparation techniques using gold foil and gold powder, and refining and separation techniques for gold and gold-silver. The scientific benefits gave a worldwide lead at that time and still have relevance in contemporary pharmacology, chemistry and metallurgy of gold.

Right from ancient times until its current use as Auranofin, gold has been used in medicines of various kinds. Many ancient cultures, such as those in India and Egypt used gold based medicinal preparations, but China was the earliest to cure sickness with it, and this could date back as far as 2500 BC (1 – 4). Since the discovery of gold, people have thought of it as having an immortal nature (*eg* resistance to chemical corrosion) and associated it with longevity. Consequently, gold was used as a medicine to seek longevity. In "On Salt and Iron" (81 BC) written by Huan Kuan of the Western Han Dynasty (202 BC-8 AD) it is stated that "immortals swallow gold and pearls, so that they enjoy eternal life in heaven and earth". Further, in the book "Zhouyi Cangtongqi" (5), written by Wei Boyang of the Eastern Han Dynasty (25-220 AD) it is recorded that "Gold is the most valuable thing in all the world because it is immortal and never gets rotten. Alchemists eat it, and they enjoy longevity". In the Eastern Jin Dynasty (317-420 AD), there was a Ge Hong (281-341 AD) who made it still clearer in his book "Baopuzi : Gold Elixir" that "gold never has any loss despite smelting a hundred times, and it never gets corroded even if deeply buried". He further added that to eat gold "tempers the body of a human being, and he enjoys eternal life". We can therefore see that although people in ancient times knew very little about the immortal nature of gold from the viewpoint of science, they were led to wonder about the effect of gold on human life. Worse still, the continuous exploration of the application of gold to the treatment of diseases also led to confusion of the two. Consequently, "medicinal gold" (man-made golden alloys and mosaic gold *etc*), and "potable gold" (the solutions of the sorts having similar colour to gold or containing gold-ion) were developed as elixirs.

This obsession and reckless pursuit by people and alchemists for gold greatly stimulated the development of the use of gold in various medicines. The alchemists' long-term effort was not successful, but it greatly contributed to the development of science and technology as a whole, including that of metals; and the development of gold drugs in ancient china was a notable achievement.

CHINA'S ANCIENT GOLD DRUGS

There are many Chinese books dealing with drug development. The most valuable of all is the "Bencao", a series of important books on Chinese *materia medica* developed continuously from the Western Han Dynasty (202BC-8AD) to the Qing Dynasty (1636-1911 AD). In all these books, gold is listed in the "mineral medicine" with details of the effects of its use. However, "Compendium of Materia Medica" (6) by Li Shizhen (1515-1593 AD) of the Ming Dynasty (1368-1644 AD) was the greatest masterpiece of all. He made a systematic summary of China's ancient gold drugs and entered it into the "metal and stone category".

Table 1 *Ancient China's Gold Drug Prescriptions*

Prescription Type*	Components	Application	Instruction
Zixuedan	Gold, *hanshui stone*, gypsum, talc, magnetite, rattletop, radix scrophulariae, licorice root, rhinoceros horn, antelope horn, agolloch eagle -wood, banksia rose, lilac, puxiao, cinnabar, musk, dangmenzi	Internal heat**, lost consciousness delirium, agitation, red tongue, sudden fainting	Cook with water
Zhibaodan	Gold foil, silver foil, rhinoceros horn, hawksbill turtle, amber, cinnabar, realgar, borneol, musk, bezoar, bezoin	Baby's sudden convulsion due to internal heat, measles, or urinary incontinence	Cook with water

* This is only a prescription-type. The percentage of medical components (including gold) is usually not provided, because the doctor of traditional chinese medicine prescribes for the patient and decides the weight of each component according to the patient's symptoms.

** The mouth is thirsty, the urine concentrated and highly coloured, stools are hard and dry, the coating on the tongue is brown, *etc*, all these symptoms arise from "internal heat" in traditional Chinese medical science.

Gold drugs were used by both physicians and surgeons.

For use in surgery, "Bencao Shujing" stated: "grind the gold into powder and apply it to the open wound of the furuncle. When it goes deep into the wound, it is capable of uprooting the furuncle entirely". In addition, "Bencao Zaixin" said that it was capable of "removing all the toxin of smallpox and skin ulcers by applying its powder to them outwardly". According to the "Compendium of Materia Medica", to remove mercury from the ear, the treatment was to "set the gold to the ear". Warm gold foil was used to remove mercury from flesh and skin. When it comes to the matter of curing sore eyes, "just burn a gold ring red hot and use it to touch the inside of the upper and lower eyelids many times a day". In the case of serious toothache, "just use a heated gold pin to give an acupuncture, and the pain vanishes immediately". Dropsy or festered sores can be treated by sucking in "qing powder" (Hg_2Cl_2), but sores of the mouth and gums were caused by this treatment. For sores of the mouth and gums, the recommendation is "just cook a gold article with water and gargle with it regularly". Although some of the procedures have a clear scientific basis and, for example, mercury is evaporated by heating, and an amalgam is formed with gold, the basis for others is less clear.

In the field of internal medicine, many medical books said that gold foil and gold powder could be used in medicine because gold had no taste and according to "the channels theory" could enter "the heart and lung channels". Some would say that it could enter "the shaoyin channels of the hand" and "the jueyin channels of the foot" (see Figures 1 (a) and (b)). By passing gold along channels in the human body, gold may be concentrated at the extremities in the hair and nails. Gold's function was to calm down the heart and confusion, detoxicate, relax palpitation, relieve craziness, stop coughing, and cure typhoid fever, and some other diseases. When "Lungs come to harm and spit out blood", "Haiyao Bencao" (7) recommended that gold therapy could be useful. People in the old days had recognized that gold could enter into the lung channel according to the "channel theory". Modern analysis found that the concentration of gold in the lung is 0.1-400ng/g (8). "Bencao Zaixin" pointed out that gold drugs are good for the joints (possibly meaning joint pains), and this can be related to modern gold medicine. In 1929, the French physician Forestier (9) for the first time successfully used the sodium aurothiopropanol sulfonate to cure rheumatic arthritis.

People in ancient times accumulated experience through endless practice, gradually leading to a combination of various medicines so as to develop a comprehensive effect which would achieve a cure. In the combination of various medicines, gold was an important component. Table 1 lists some of the prescriptions containing gold.

It is worth mentioning that *zixuedan* (see Table 1) was regarded as being as effective as *niuhuang qingxinwan* in curing the measles. Both had the reputation of being able to remove "internal heat" from the body (see Table 1**). All these prescriptions

can be regarded as "the gold prescription" of traditional Chinese medicine. According to modern analysis, the horns of the rhinoceros and antelopes and other animals contain traces of gold. For example, the gold content in the ashes of deer horn is 60 – 80 μg/g (8) and the gold content in ashed horn of *odocoileus hemious* is 0.3 – 28.3 ng/g (10). Boyle considered that the gold concentrates mainly in protein (*eg* horn, hair) possibly as gold-protein complexes (11). Many medicinal herbs contain a trace of gold (12) and their extracts might contain a trace of a gold complex that could cure the sickness.

CHINA'S ANCIENT "MEDICINAL GOLD"

Arising from the fact that people had a thirst for gold treatments, and that gold was linked to the mystery of life, alchemists devoted themselves to the manufacture of the Elixir for immortal life and tried to produce man-made "gold". That is, they melted together the Cu, Sn, Pb, and some other metals to make a golden-coloured alloy or made mosaic gold (golden-yellow SnS_2 crystals), *etc* (13). In "Baopuzi: The Internal Chapter – Yellow (Gold) and White (Silver)", Ge

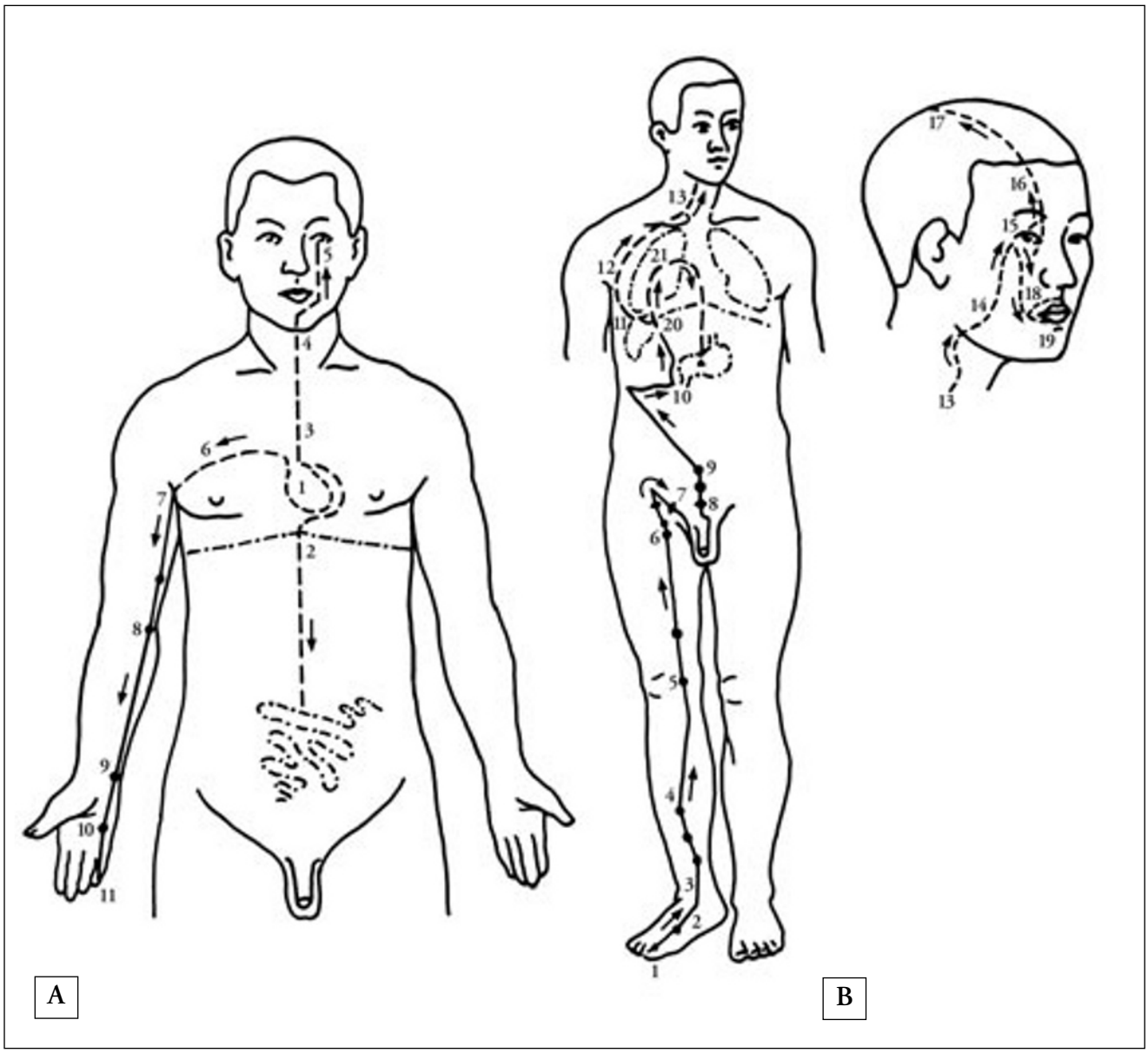

Figure 1 *According to the "channels theory" of traditional Chinese medicine, gold could enter (a) the shaoyin channels of the hand or (b) the jueyin channels of the foot. The arrows indicate the path for gold along the body channels*

Hong said, "Since there is gold in heaven and earth, I can do it. Two yellow and one red (*ie* red HgS), and gold is made from these immediately without doubt". The earliest literature on the "transformation into the gold" in making the Elixir was "Records of the Historian-Basic Annals of the Emperor Xiaowu", which said that, "cinnabar can be transformed into gold", and thus the gold transformed was the "elixir of life". When it came to the Sui Dynasty (581-611, AD), the alchemist Su Yuanming recorded 15 kinds of "medicinal gold" in his book "Discourse on the Contents of the Precious Treasury of the Earth". The "Compendium of Materia Medica" recorded all of them, but pointed out that they were all fake gold made from various "medicines". China's "yellow and white technique" was approaching its perfection from the earlier years of the Western Han Dynasty to the earlier years of the Sui Dynasty, and the varieties were greatly increasing. According to Ge Hong of the Eastern Dynasty, "medicinal gold" was better than real gold, and "the gold thus transformed is the essence of all the medicine, much better than all the natural drugs". The alchemist Zhang Jiugai of the Tang Dynasty (618-907AD) also praised "medicinal gold" in his "On the Gold and Stone Spiritual Sands", which said that "medicinal gold" was "an immortal medicine". Zhao Kuanghua *et al* (14) carried out extensive research on China's "medicinal gold" and "medicinal silver" and concluded that the "medicinal gold" listed in "On the Gold Stone Spiritual Sands" was "mysterious" and "non-existent at all". In fact, the term itself had begun to vanish after the Tang Dynasty. The reason might be that Li Shizhen had pointed out that "fake gold is poisonous. It is silly that you wish to cure your sickness with it and the result was just the contrary". However, despite the failure to make a drug conferring immortality or to transform their preparations into real gold, their contribution is worth noting. Zhao Kuanghua *et al* (14) had made a series of textual searches for medicinal gold and silver and these are summarized in Table 2. Although the alchemists' ultimate objective was absurd, they were successful in making "imitation gold" powders such as Cu-Zn powder and SnS_2, *etc.* Thus, the evolution of "medicinal gold" did contribute to the science of materials.

Table 2 *Chemical Composition of "Medicinal Gold" Preparations in Ancient China's Alchemy*

Name of Material	Results of Textual Search (14)
Malerealgar gold	Cu-As (10%) alloy or SnS_2
Orpiment gold	ditto
Tou shi gold ("brass gold")	Cu-Zn alloy
White tin gold	SnS_2 (coloured gold)
Zengging gold	Cu-Hg overlaid with a layer of Fe_2O_3
Chalcanthite gold	ditto
Sang gold	
Greenish brown sand gold	
Black lead gold	PbO (red lead) possibly containing Pb_3O_4
Cinnabar gold	Still to be verified

ANCIENT CHINA'S "POTABLE GOLD"

"Potable gold" is referred to as "drinkable gold". Since gold flakes or powder and "medicinal gold" are "heavy articles" which cannot stay long in the "stomach and guts", and were in some cases toxic, alchemists sought to solve the problem by making "drinkable gold" as an elixir. In fact, alchemists in both East and West were all engaged in the making of potable preparations of gold. The earliest literature dealing with potable gold in China was "On Salt and Iron" written in 81 BC. Later, many books mentioned it in various contexts, emphasizing that potable gold was an important elixir.

Which chemical elements does "potable gold" contain? Does it contain any soluble gold? As classified by its main raw materials, "potable gold" can be divided into three categories: gold, other metals and alloys, and sulfur. Modern science indicates that gold dissolves in water only when there are ligands present and it is in an oxidized state.

Meng Naichang *et al* (15) made some simulated tests on prescriptions for "potable gold" written in ancient works. The original prescription for "potable gold" carried in the "Taiqing Potable Gold Elixirs" was as follows: "Put 9 liang (a unit of weight in ancient China) of gold into bitter wine for a hundred days ... and you will get potable gold ... the essence all goes into it". In "36 Ways for Making Potable Gold", the prescription ran as follows: "Put half a kilo of gold and a kilo of green vitriol into a green bamboo tube and seal the mouth tight. Then put it into a pool, and in 50 days you will get potable gold". The prescription for making potable gold written in "Baopuzi: The

Table 3 *Concentrations of Gold in Elixirs (15)*

Gold (g)	KCN (g)	20% HOAc (ml)	Other Components (g)	Days Kept	Colour of the Solvent	Au^{3+} (g) in the Solution
1 0.2594	0.2004	25	Realgar, 1.0038 NaCl, 1.0034 Sulfur, 1.0026 KNO_3, 1.0000 Fe_3O_4, 1.0049 Cinnabar, 1.0021	8	Light brown	7.95×10^{-6}
2 0.2535	0.2160	25	———	8	Colourless	45.1×10^{-6}
3 0.2532	0.2048	25	$CaSO_4$, 1.2131 $MgSO_4$, 0.3635	8	Tangerine	16.1×10^{-6}
4 0.2638	0.2136	25	$Fe_2(SO_4)_3$, 1.0026	8	Tangerine	4.8×10^{-6}
5 0.2450	0.2082	25	$FeSO_4$, 1.0058	8	Red	19.6×10^{-6}

Internal Chapter" (13) was: "take half a kilo of gold with an old balance and seal it with vinegar, raspberry, Taiyi xunshou zhongshi, (an alchemists term for As_2S_2), ice stone, ziyounu, (this could be S, $Fe_2O(SO_4)_2$, $FeSO_4 \cdot 7H_2O$ or NaCl), xuanshuiye, (Fe_3O_4 or Hg), cinnabar, and jinhuashi, (KNO_3), and you will get potable gold". Meng (15) did not find gold soluble in the prescription written for making "Taiqing Potable Gold Elixirs" when he followed the instructions. He also made simulated experiments on the "36 Ways for Making Potable Gold" and found that if the green vitriol was oxidized to a certain extent in the air, and in the presence of a certain proportion of the three-valent ferric-compound, there would be some chloride impurities:

$$Au + 3Fe^{3+} + 4Cl^- \rightarrow [AuCl_4]^- + 3\ Fe^{2+} \qquad (1)$$

Although the ancient alchemists knew little about chemistry they were thus able to make potable gold. Meng Naichang *et al* (15) made further simulated tests on the potable gold prescribed in "Baopuzi: The Internal Chapter". They carried out five experiments on the other prescriptions (see Table 3) and found that there really was some gold dissolved in the "potable gold".

We now know that cyanide is present in over a thousand plants, and some of the traditional Chinese herbs used for medicine are amongst these. Fresh raspberries contain cyanide and this is the key factor enabling dissolution of gold in the prescription "Baopuzi: The Internal Chapter" for potable gold (13).

Meng Naichang *et al* (15) were already aware of the small amounts of cyanide contained in the fresh raspberries, and so they added 0.2g KCN to make an enlarged simulated test, as follows.

Gold dissolves in cyanide according to Equation (2):

$$4Au + 8CN^- + O_2 + H_2O \rightarrow 4[Au(CN)_2]^- + 4OH^- \qquad (2)$$

If acetic acid and potassium cyanide are mixed, they will react to form HCN and potassium acetate; but in alkaline solution the complex ion does not change and reaction (3) takes place:

$$4Au + 8CN^- + O_2 + 4HOAc \rightarrow 4[Au(CN)_2]^- + 4OAc^- + 2H_2O \qquad (3)$$

The above considerations indicate that "potable gold" was in fact likely to contain a very small amount of dissolved gold.

The cyanide concentration in plants is usually ng (ppb) range. The use of 0.2g KCN in simulated tests is reasonable even although the concentration is actually several orders of magnitude greater than in the comparable volume of raspberry puree or juice, because this enables a qualitative conclusion to be made which can be regarded as an indication of what might have taken place in the ancient Chinese experiments.

CONCLUSIONS

The earliest application of gold as a therapeutic agent originated in China, and gold was widely used by ancient physicians and surgeons. People in the old days accumulated experience through endless practice, and

gradually developed useful gold drugs. Some of them had a reputation for having a good therapeutic effect. Ancient China had remarkable achievements in this field; and some of these gold drugs had a relationship to their modern successors.

In order to use pure gold for drugs, techniques were developed in the second century AD for refining gold and for separating gold – silver alloys. In order to use gold powder for drugs, techniques for making gold foil and powder were devised by alchemists (16, 17). Due to the fact that people were so obsessed with gold, and with the great value of gold, alchemists began to produce man-made "gold". Though their objectives were absurd, they were successful in making a variety of imitation gold materials, and had a deep understanding of the Au-Ag system, and also the Au-Cu, Cu-Zn, Cu-As, Cu-Hg, Sn-S and Hg-S *etc* systems.

Ancient alchemists in China even found chemical species which help in the dissolution of gold (*ie* Fe^{3+}, and Cl^-) and also used cyanide-containing plants to dissolve gold; and both their metallurgical and chemical achievements were therefore considerable.

ABOUT THE AUTHORS

Professor Zhao Huaizhi was Director of the Kunming Institute of Precious Metals in China from 1984-1994 and is now Editor-in-Chief of 'Precious Metals', a journal which is published quarterly from the Institute (in Chinese). He has worked for many years with precious metal materials and was awarded the third national prize for invention (China). He has always been interested in the research, development, applications, and history of gold.

Professor Ning Yuantao is a Research Fellow at the same Institute, working on a variety of research projects related to precious metals materials. He has considerable scientific achievements and has won national prizes. His work has also been concerned with research into applications for gold and its alloys.

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