Saltpetre in Early and Medieval Chinese Medicine

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Abstract
Saltpetre, xiaoshi (消石), was used extensively in early and medieval Chinese medicine for the treatment of a number of common ailments and as a general aid to good health. Until recently it was thought that saltpetre had no biological action except as a diuretic, but recent research suggests that this is not the case. Some of the claims made by Chinese physicians are consistent with current scientific understanding.

Keywords
Saltpetre, xiaoshi, dietary nitrate, nitric oxide, saliva, angina pectoris, hypotensive agent, Shen Nong bencao jing, Mawangdui, Dunhuang, glyceryl trinitrate, cow lick

By the end of the third century BCE Chinese medicine was emerging from the use of charms and spells and acquiring elements that we might now recognise as evidence-based medicine.\(^1\) Among the treatments available, herbs, animal products and minerals were prescribed for various common ailments. Chinese herbal remedies we still have with us but the use of minerals has diminished, in spite of its importance in former times.\(^2\) One of the minerals used frequently in China for medical purposes was xiaoshi 消石, commonly identified as saltpetre (also called nitre), better known today as a component of gunpowder, possibly China’s most significant invention.\(^3\) However, the mixture of saltpetre, charcoal and sulphur was not compounded in the search for an explosive but in the hope that it might have therapeutic value.

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\(^1\) For the history of medicine in early China, see, for instance, Unschuld 1985, chapters 1–3, and Yamada 1998.


\(^3\) The history and development of gunpowder and the use of saltpetre in China is dealt with at length in Needham 1986. He also discusses saltpetre, especially its uses in alchemy, in Needham 1980.
Xiaoshi was classed in the highest of three grades of materia medica in the *Shen Nong bencao jing* 神農本草經 (*The Divine Husbandman’s Classic of Materia Medica*), the earliest and most revered pharmacopoeia in the Chinese tradition, probably compiled by the second century CE. This puts it in the class of elixirs, and, as another later and now also lost text, the *Mingyi bielu* 名醫別錄 (*Informal Records of Eminent Physicians*) of Tao Hongjing 陶弘景 (456–536) puts it, it is ‘a miraculous product of Heaven and Earth’. Recent physiological research has shown why this classification has some validity.

First, though, we must consider the identification of what the ancient Chinese called xiaoshi as saltpetre. It is, of course, routinely identified as such in all modern reference works. However, several authors have discussed the problems of the identification of Chinese materia medica, and xiaoshi in particular, and the application of modern scientific nomenclature to them. Indeed, in the largest of all the Chinese traditional materia medica, *Bencao gangmu* 本草綱目 (*Compendium of Materia Medica*, first printed in 1596), Li Shizhen 李時珍 (1518–1593) has a long passage concerning the problems of distinguishing between xiaoshi and other salts, in particular mangxiao 芒消 (sodium sulphate, Glauber’s salt). His lengthy discussion attempts to clarify the situation by largely using crystalline form to distinguish between the substances. This is not very satisfactory as, although the substances have different crystal symmetries, the phenomenon of polymorphism renders the criterion of crystalline appearance totally unsatisfactory. However, long before this, the Chinese had discovered a fool-proof test to distinguish saltpetre from the others: the flame test, well-known to all who studied chemistry before the demise of the Bunsen burner. This is first mentioned at the end of the fifth century CE by Tao Hongjing in a context that suggests that it had been known about for some time. He states that when heated xiaoshi (if it is saltpetre) ‘produces a purple smoke’. This would not be the case with the sulphates of sodium and magnesium. Subsequently, from the ninth century onwards, as knowledge and use of gunpowder spread, the production and purification of saltpetre came to be taken very seriously by the

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4 The *Shen Nong bencao jing* only survives as quotations, and has been reconstituted in Ma 1995. For xiaoshi, see p. 157. For the dating of the text, see also Unschuld 1986, pp. 11ff.
9 Discussed in Needham 1980, p. 185ff.
They must thus have known more about saltpetre than most other minerals.

However, because of the confusion of nomenclature it is probable that some early Chinese physicians used sodium or magnesium sulphate when they should have used saltpetre, but no cure would have been effected as the physiological effect of the sulphates is completely different from that of saltpetre. Presumably they would have put down the lack of a cure as one of the failures common enough in medical practice even today. As physicians rarely report their failures nothing more would have been heard of it. When the physician got it right and used saltpetre in the treatment it would have been reported and the physician would have reaped the appropriate reward.

Saltpetre is potassium nitrate (KNO₃) and the nitrate ion (NO₃⁻) is a particularly benign chemical species. For this reason it is one of the forms in which excess nitrogen from ingested protein is excreted from the body in urine. Until recently nitrate was thought to have no biological action, except as a diuretic. However, its close relative, the nitrite ion, with just one oxygen atom fewer (NO₂⁻), is very different and it has a number of biological actions, some of them well-established, others the subject of intense research at this time. Concerning the former, nitrite has antibacterial activity and has been used for many years as an additive in preserved tinned meat because of its toxicity towards Clostridium botulinum. There is nitrite in human perspiration that probably kills pathogenic bacteria and fungi on the skin. Current research mainly concerns nitrite as a hypotensive agent. It is chemically closely related to nitric oxide (NO), a molecular species that acts as a messenger molecule in controlling the relaxation of vascular smooth muscle and, therefore, blood vessel dilation, thus playing a major role in the maintenance of optimal blood pressure. The discovery of this important and totally unexpected role for nitric oxide was awarded a Nobel Prize in 1998. With hindsight nitric oxide is not such a surprising molecule for bringing about blood vessel dilation as amyl nitrite and glyceryl trinitrate have been used in the treatment of angina pectoris for many years. It might be thought that the use of saltpetre in Chinese medicine parallels the use of glyceryl trinitrate in Western medicine because of the presence of the nitrate moiety in both, but the situation is much more complicated than this. Glyceryl trinitrate, a covalent compound, is converted enzymatically into nitric oxide in vascular tissue but this is not the case with the nitrate ion.

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Nitric oxide is synthesised in many tissues by the action of an enormously complex enzyme, nitric oxide synthase, on a combination of two substrates, the amino acid arginine and molecular oxygen. In tissue depleted of oxygen this mode of synthesis cannot occur, but blood vessel dilation is still required to enhance the flow of oxygenated blood to tissue where the oxygen is required. Under these circumstances another substrate is used for the enzymatic generation of nitric oxide and this is thought to be the nitrite normally present in blood plasma. Aside from the laboratory evidence to support this view, it has been noted that Tibetan highlanders, who are permanently starved of oxygen, have higher than normal levels of nitrite in blood plasma. So, nitrite is hypotensive because of the ease with which it can be converted into nitric oxide. But nitric oxide is much more than a hypotensive agent. It is one of the toxic agents produced by the immune system, it is a neurotransmitter, a messenger molecule in the brain as well as an agent for enhancing the process of wound healing. For nitrate to generate nitric oxide it must first be converted into nitrite.

There are at least four ways in which this transformation might come about and we need to evoke all of them to understand why Chinese physicians might have found saltpetre a valuable medicine.

1. Heat will readily effect the conversion of nitrate into nitrite:
   \[ 2\text{KNO}_3 \rightarrow 2\text{KNO}_2 + \text{O}_2 \]
   This is its role in gunpowder, giving a copious supply of oxygen to enhance the conflagration of sulphur and carbon to the appropriate gaseous oxides. Tudor medicine in Europe, which also used saltpetre, knew that heating it made it more powerful and Chinese physicians often heated drugs to ‘strengthen’ them.

2. There are enzymes in the mouth, particularly under the tongue, that convert nitrate into nitrite (the nitrate reductases, step ii in Figure 1), so that mastication of food enhances the nitrite level in plasma as most foods, particularly vegetables, contain nitrate.

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16 Challoner 1584, pp. 1–58.
17 Srivastava et al. 1982, pp. 400–1.
Saltpetre is produced spontaneously from the decay of organic matter by the use of a number of bacterial enzymes (see Figure 1). The final product (nitrate) appears as an efflorescence on the ground. If step i is not complete then it will be contaminated with nitrite. If the saltpetre comes from older deposits then this is unlikely as nitrite is slowly oxidised to nitrate by air.

Nitrite in solution under even mildly acid conditions will generate nitric oxide.

Although there are old deposits of saltpetre in China, most saltpetre seems to have been obtained as a seasonal efflorescence due to the decay of nitrogenous organic matter in the naturally occurring nitrogen cycle shown in Figure 1. The harvesting of saltpetre from the surface of soil is described in many ancient Chinese texts. For example, the *Mingyi bie lu* (*Informal Records of Famous Physicians*), already quoted above, says of saltpetre:

> Nowadays, in the mountains north of Dangchang there are places with salty earth which produce it.

The sixteenth-century Chinese manuscript shown in Figure 2 gives instructions for the purification of saltpetre, but this process would not have resulted in any contaminating potassium nitrite being removed.

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Fig. 2. Instructions for the purification of saltpetre. From chapter 1 (p. 154) of the late sixteenth century manuscript work *Buyi Lei Gong paozhi bianlan* (Handbook of the Supplement to Lei Gong’s Methods of Preparing Medicines) Shanghai: Shanghai cishu chubanshe, 2005.
Let us now turn to some examples of the use of *xiaoshi* in Chinese medical recipes on which the description of the medical properties of saltpetre may shed some light. In 1973, excavations of tomb no. 3 at Mawangdui, Changsha unearthed texts written on silk, one of which consisted of medical recipes, the *Wu shi er bing fang* 五十二病方 (Recipes for 52 Ailments). The tomb was sealed in 168 BCE, though the text may date to the third century BCE. There is an authoritative study and translation by Harper.\(^{23}\) Recipe 16 is a treatment for a sore or infected wound:

一消石置溫湯中以灑癰

The sixth character (*tang*) appears to have been used at that time to mean hot water. Harper gives as the translation:

Place the saltpetre in hot water and wash the sore with it.\(^{24}\)

If the saltpetre contains some nitrite this could act as an antibacterial agent to treat the infection. Also, as mentioned previously, nitric oxide is generated from nitrite in an acidic environment and the pH of skin is quite low. The nitric oxide produced would speed up the process of wound healing.

Another treatment for a wound is given in Recipe 46:

一濡以鹽傅之令牛舐之

Harper translates it as:

Moisten it, spread salt on it and have a cow lick it.\(^{25}\)

The salt encourages the cow to lick it and, according to Harper ‘having a cow lick the wound is a kind of magical treatment’, quoting other examples from later texts in support of this.\(^{26}\) However, a cow’s saliva may also contain enough nitrite to speed up wound healing. Licking a wound is, of course, a common treatment and there are other therapeutic agents in saliva apart from nitrite.\(^{27}\)

One of the most intriguing collections of Chinese medical manuals comes from the cache of manuscripts found in the Buddhist grotto at Dunhuang and first reported by Aurel Stein in his exploration of central Asia in 1910. The manuscripts, largely of Buddhist origin, had been secreted in a cave in


\(^{25}\) Harper 1998, p. 239.


\(^{27}\) Root-Bernstein and Root-Bernstein 1999, pp. 110–18.
about 1000 CE and walled up to protect them from the Islamic invasion of the region. Over the years around 20,000 manuscripts were removed, mainly by European visitors, and lodged in museums all over the world, including many in the British Museum. A number of the manuscripts in the cache dealt with medical matters and one ended up in the hands of a Chinese physician living in Hebei province. He made two copies of the manuscript for teaching purposes and, although the original was destroyed during the Cultural Revolution, one copy has survived. Internal evidence suggests that the original was written in the eighth century CE. It has been translated by Moffett:

着舌以通心气
Putting under the tongue to cause heart qi to flow freely

治中恶急心痛手足逆冷者顷刻可杀
For treating symptoms such as struck by evil, acute heart pains and cold in the hands and feet which can kill a patient in an instant

看其人指爪青者是
Look at the patient’s fingers and those with greenish black nails are such cases

硝石五钱匕 雄黄一钱匕
Saltpetre (5 spoonfuls) and realgar (1 spoonful)

右二味共为极细末启病者舌着散一匕于舌下若有涎出令病者随涎咽下
Combine these two into a fine powder. Lift the patient’s tongue and sprinkle 1 spoonful under the tongue. If saliva is produced have the patient swallow it.

必愈
This is a certain cure.

The condition described is almost certainly some type of cardiac dysfunction, probably angina pectoris. Holding saltpetre under the tongue will, of course, convert nitrate into nitrite due to the presence of nitrate reducing bacteria, probably there to provide some antibacterial action in the mouth. Nitrite, when taken into the blood stream provides the hypotensive action necessary to relieve the painful symptoms of angina. The very precise instructions in terms of holding the saltpetre in the mouth and swallowing the saliva (thereby maximising the amount of nitrite ingested) indicate the acute observational powers of early Chinese physicians. Without that procedure there is no cure. Chinese physicians also had great regard for the medicinal value of

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29 Lo and Cullen 2005.
30 The manuscript is entitled Fuxing jue zangfu yongyao fayao 蘇行訣臟腑用藥法要 (Assisting the [Five] Phases Rhymed Formulae of Essential Methods of Using Drugs for the Internal Organs). For background and dating of the manuscript, see Ma 1998, p. 195ff. The recipe translated below can be found on p. 194, lines 9–13.
realgar (arsenic sulphide) because it is the colour of healthy blood, hence its inclusion in the above recipe. However, because of its extreme insolubility, it would have had no effect on the patient.

Already mentioned above, the largest of all the Chinese traditional materia medica is the Ben cao gangmu 本草綱目 (Compendium of Materia Medica) of Li Shizhen, published in 1596. For a study of the history of Chinese prescribing it has the advantage of summarising many previous materia medica and its entry on saltpetre is extensive and of great value. Much of it is taken up with a discussion of which minerals really are saltpetre, as there was some confusion with sodium sulphate (Glauber’s salt) and other salts. Near the end of the entry, Li provides an account of the therapeutic uses of saltpetre. As in other entries, he quotes and comments on general accounts of its therapeutic functions from a selection of previous works that he considers to be of value. One such example is this, from the Shen Nong ben cao jing (The Divine Husbandman’s Classic of Materia Medica):

It eliminates accumulated Heat in the Five Viscera, relieves distention of the stomach, clears away the accumulation of indigestion, pushes away the old and brings in the new, and disperses pathogenic factors.

He then concludes the entry with some 14 prescriptions culled from a variety of sources. Some of these make little sense beyond the context of medical concepts of the time, such as treating black jaundice due to overexertion during sex, or treating a hard mass in the abdomen due to invasion by a dragon. Others, however, when considered in the light of the recent developments in our understanding of the potential physiological effects of saltpetre outlined above, may reflect hard-won empirical knowledge acquired over generations.

Prescription 11–11–1, taken from Lei Gong pao zhi lun 雷公炮炙論 (Lei Gong’s Treatise on the Preparation of Drugs, a text originating in the fifth century CE with additions up to the ninth) for treating severe headache that makes the patient feel he is going to die:

Blow saltpetre into the nostrils. This will relieve the pain.

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32 A full English translation of this work has only recently become available (Li 2004). The first book-length English language monograph on the work has also recently been published (Nappi 2009).
35 Li 1975, pp. 654–5; 2004, pp. 1178–80. For ease of reference the numbering of these prescriptions used in Li 2004 has been adopted.
36 There is considerable debate over the dating of this text, see Unschuld 1986, p. 239, Shang 1989, pp. 170–1.
Much nitric oxide is produced in the nasal passage and providing nitrite as a substrate for NO-producing enzymes could enhance NO production. Gladwin et al. found that inhaled nebulised sodium nitrite is a pulmonary vasodilator and so might ameliorate the congestion that can be the cause of a headache.

Prescription 11–11–4, taken from the *Tai ping shenghui fang* (Benevolent Prescriptions of the Taiping Era, a text of the late tenth century CE) for treating inflamed eye with pain and swelling:

Insert powder of saltpetre as small as a millet seed with a copper stick into the canthus (of the eye) before sleeping. Wash it away next morning with salt water.

The antibacterial activity of nitrite could reduce the infection. Rather curiously, copper can reduce nitrite to nitric oxide by chemical means and so the insistence on the use of a copper stick may be significant.

Prescription 11–11–5, taken from *Zhang Sanfeng xian fang* (Zhang Sanfeng’s Immortal Prescriptions) as a treatment for nubulae and opacity. The prescription claims to restore eyesight by the use of saltpetre, but it is interesting that again the author specifies the use of copper vessels.

Earlier in the entry, Li also records a perceptive remark made by Da Ming, a tenth-century physician and author of *Rihuazi bencao* (The Sun-rays Master’s Materia Medica). Da says of saltpetre:

Hold the drug in the mouth and swallow the liquid little by little to treat inflammation of the throat.

Utilising the nitrate-reducing bacteria of the mouth is a more certain way of ensuring the drug’s antibacterial activity than relying on adventitious amounts of nitrite in the saltpetre. Da Ming was wiser than he realised.

Although it would appear that saltpetre has value, under certain conditions, in the treatment of various ailments the Chinese claimed for it far more than this. Indeed another lost work quoted in the *Bencao gangmu*, the alchemical text *Sheng Xuan zi fugong tu* (Master Sheng Xuan’s Chart for Subduing Mercury), says:

Take a decoction of the drug to prolong life.

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41 Li 1975, p. 650; 2004, p. 1172.
This claim would, until recently, have occasioned doubt or even derision. However, a research paper in no less a journal than *The New England Journal of Medicine* reports a recent Swedish study on the benefits of consuming nitrate on the blood pressure of healthy volunteers. Ingested nitrate is concentrated ten-fold in the salivary glands and undergoes an enterosalivary circulation where it is converted into nitrite. In view of the serious consequences of chronic hypertension any therapy that lowers blood pressure could be said ‘to prolong life’.

To conclude, it is instructive to compare remarks on the value of saltpetre made about 1800 years apart. The first is in a 2008 issue of the journal *Hypertension*:

we advocate consumption of a diet high in nitrate... to protect individuals at risk of adverse vascular events.

The second is from the *Shen Nong bencao jing* of the second century CE:

Long-term taking of nitrate lightens the body.

A ‘light body’ in this case meant being in perfect health and closer to being an immortal. It is now possible to take in extra health-giving nitrate by drinking organic beetroot juice but this is really no advance on the Chinese who took a little *xiaoshi* to prolong their lives.

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