SHORT COMMUNICATIONS

The composition and origin of massicot, litharge (PbO) and a mixed oxide of lead used as a traditional medicine in the Arabian Gulf

Michael A. Worthing

Department of Earth Sciences,
Sultan Qaboos University,
Box 36 Al-Khod 123,
Muscat,
Sultanate of Oman

Hector H. Sutherland

Department of Physics,
Sultan Qaboos University,
Box 36 Al-Khod 123,
Muscat,
Sultanate of Oman

LEAD and lead minerals have been used for medical purposes throughout human history. For example, galena was used as an eye salve in pre-Dynastic Egypt and by the ancient Indian civilisations of Mohendro-Daro and Harappa some 3200 to 2800 B.C. (Nriagu, 1983). The use of lead and other heavy metals and their compounds in Ayurveda, the Hindu system of medicine, can be traced back to the first century A.D. when Jain and Buddhist healers began to encourage the use of these substances instead of animal products (Mukherjee, 1992). Minerals were used in the preparation of many of the Ayurvedic medicines (Murthy, 1983). These ancient practices spread and have continued into modern times. For example, contemporary use of lead compounds in traditional medicine has been reported by Bose et al. (1983) and Cueto et al. (1989).

In the Arabian Gulf, the substance bint al dhahab (English 'daughter of gold') has been used as a traditional medicine, probably for centuries. It is given to new-born babies and small children for clearing the meconium and for stomach ailments. A small quantity is powdered, mixed with butter and sugar and given to the child on the end of a finger. It has been known for some time that it consists dominantly of lead oxide (McNeil and Reinhard, 1967) and medical studies have shown that the polymorphs of PbO, massicot and litharge are present (Woolf, 1990). Recently it has been linked with cases of acute lead encephalopathy in infants 2–4 months old (Woolf et al., 1990) and the Omani Government has banned it. However, it is still available in the souks of Oman, the United Arab Emirates and Bahrain. Local traders say that it comes from Iran. The purpose of this paper is to present new data on its composition and to suggest a possible manufacturing process and origin.

Materials and methods

Four specimens were studied, three purchased in Oman and one from Bahrain. In hand specimen the substance has the high specific gravity characteristic of lead-bearing minerals and consists of a mass of

interlocking golden- to honey-coloured acicular crystals up to a few millimetres in length. Some specimens are bounded by curved surfaces suggesting contact with the sides of a crucible. Others have circular to elliptical gas bubbles which were frozen into the specimen during cooling. Some specimens also have flat surfaces which probably represent the top open surface of the crucible charge. These observations suggest that the substance was produced from some primary mineral which has been heated in a crucible.

Three samples were cut from a block showing both the curved and flat surfaces described above. The samples were cut in such a way that they represented different depths below the top of the crucible charge assuming the flat surface to be the top. The samples were mounted in araldite and polished. When viewed on the scanning electron microscope the specimen appears as a radiating mass of acicular to lath-like crystals (Fig. 1). Three separate mineral phases are present. They are denoted here A, B, and C (Fig. 1). Phase A tends to occur as larger prismatic phenocrysts, phase B as radiating acicular crystals and phase C fills the interstices between the other two phases. The textural relationships suggests an order of crystallisation. The more coarsely crystalline appearance of phase A (Fig. 1) indicates early crystallisation while the more acicular radiating form of phase B resembles the quench textures common in volcanic rocks and suggests rapid cooling at lower temperatures. The interstitial occurrence of phase C suggests that it crystallised from the residual liquid left after crystallisation of phases A and B. The general grain size of the minerals decreases slightly downwards into the charge but the relative amounts of the three phases appears to be unchanged.
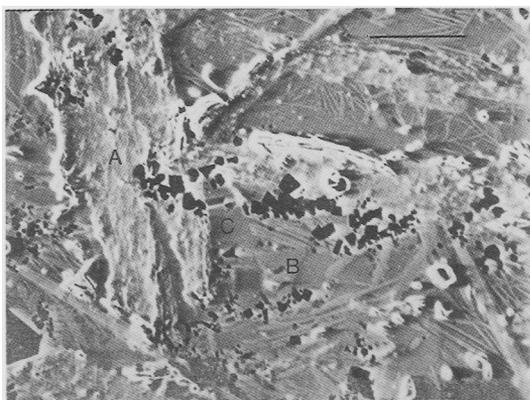

FIG. 1. Backscattered scanning electron photograph of phases A, B, and C. Bar scale is 25 μm.

The composition of the substance was studied using four techniques; X-ray diffraction and electron microprobe, inductively coupled plasma emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GFAAS).

X-ray diffraction. The samples were powdered under acetone in an agate pestle and mortar and run on the Philips PW 1710 X-ray diffractometer in the Department of Earth Sciences at Sultan Qaboos University. The on-line JCPDS data file identified the two polymorphs of PbO: litharge and massicot, but failed to identify the third phase. However, this phase appears to be crystalline as it consistently gives well defined peaks on the scans. Experimental work by Peterson (1941) and White *et al.* (1961) has shown that the red to reddish yellow tetragonal litharge is stable at ordinary temperatures and massicot, the yellow orthorhombic form is stable above 489°C. The presence of the high-temperature massicot in the substance supports an origin by the heating of some primary lead-bearing substance in a crucible.

Electron microprobe. Determinations of the mineral chemistry were done on the wavelength dispersive system of the Cameca Camebax SX 50 X-ray microanalyser at the Central Science Laboratory at the University of Tasmania. Operating conditions included an accelerating voltage of 20 kV, a beam current of 20 nA and a livetime of 80 seconds. Detection limits were of the order of 0.1%.

Selected chemical analyses are presented in Table 1. Compositions of Pb oxides were calculated assuming two valencies for Pb (2 and 3). The most satisfactory totals were obtained using divalent Pb which is consistent with the X-ray diffraction trace which suggests that the dominant oxide of lead is PbO. The compositions of phases A and B are identical suggesting that they are the two polymorphs of PbO, litharge and massicot. The textural and phase relationships for the polymorphs of PbO discussed above suggest that the higher temperature phase A is massicot while phase B is the lower temperature litharge. The composition of phase C is more complex. It contains significant amounts of Si, Al, Fe, K and Sb and the analyses (Table 1) and element distribution maps for Si and Al clearly show that these elements are associated with phase C suggesting that it is a complex oxide of lead with the other elements held in solid solution. The K in phase C may have been derived from jarosite $(K_2Fe_6(OH)_{12}(SO_4)_4)$, a common secondary mineral found associated with lead deposits.

The average bulk analysis (Table 1) represents the average composition of eleven 50 μm diameter fields. This analysis is thus the most significant medically because it represents the average composition of the material ingested by patients. These data show that the substance contains significant amounts

TABLE 1. Selected analyses of phases A, B and C

Wt.% Oxide	Phase A	Phase B	Phase C	Average Bulk
PbO	101.389	100.706	87.131	91.796
SbO	0.078	0.099	0.698	0.599
SiO$_2$	0.008	0.015	8.933	5.348
TiO$_2$	0.056	0.072	0.159	0.057
Al$_2$O$_3$	0.001	0.000	0.671	1.213
FeO	0.000	0.027	1.994	0.941
CaO	0.001	0.000	0.050	0.052
K$_2$O	0.000	0.000	0.070	0.500
CuO	0.017	0.000	0.180	0.111
SO$_3$	0.000	0.000	0.175	0.070
Total	101.550	100.919	100.061	100.687

Trace elements ppm

Ba	3000
Ti	3000
Cd	508
As	300
Ag	1
Zn	n.d.
Au	n.d.

Average Bulk = average of eleven 50 μm fields.
n.d. = not detected.
See text for explanation of methods.

of antimony oxide (SbO) as well as oxides of lead (PbO). In addition, eight 50 μm fields were analysed for cadmium and arsenic. These analyses showed that an average of 508 ppm of cadmium are present (range 403 to 724 ppm). No arsenic was detected.

ICP-AES and GFAAS. The trace element content of one sample was investigated using an ARL/ FISONS 3560 ICP-AES and a Perkin Elmer 2380 GFAAS at the Ministry of Petroleum and Minerals Analytical Laboratory, Sultanate of Oman. 0.5 g of sample were dissolved in 20 ml of nitric acid by warming on a hotplate. The resulting solution was brought up to 50 ml with distilled water in a volumetric flask and run on the machines which have detection limits of 1 ppm. As, Ba, Ti and Zn were investigated by the ICP-AES and Ag and Au by GFAAS. Approximately 300 ppm As were detected by the ICP-AES (range 295—325 ppm). The results are given in Table 1.

Discussion

In nature massicot and litharge occur as oxidation products of galena and other lead minerals in gossans (e.g. Karup-Møller, 1975; Van Moort and Swensson,

1982). Available data suggest that although massicot is a relatively common mineral in gossans it occurs in very low modal abundances, generally less than 1% (Blanchard, 1968). It appears unlikely therefore, that primary massicot is the source of bint al dhahab. Moreover, the structure of the specimens described above suggests that bint al dhahab is not a primary mineral but has been produced by the heating of a precursor in a crucible. A possible candidate for this precursor is cerussite which can be abundant in the gossans of lead deposits (Blanchard, 1968; Van Moort and Swensson, 1982). For example, data from Blanchard (1968) suggest that it may comprise up to 10% of the ore deposit mode. Cerussite starts to breakdown at 130°C to form PbO and decomposition is complete at 470°C (Abel, 1975). Galena (PbS) sublimes unchanged at 1000°C and boils at 1200°C (Abel, 1975) and cannot therefore be the primary mineral from which bint al dhahab is made. Likewise anglesite (PbSO$_4$) melts at 1170°C (Abel, 1975).

In association with mining and smelting activity, Milton (1955) described massicot and litharge as well as metallic lead, copper and silver in llama bones from Bolivia. The bones appear to have been used instead of bone ash during smelting of lead–copper ores. Friedlaender and Choo (1970) tentatively identified massicot in slags from Zawar mine, Rajasthan, India. However, Freestone *et al.* (1991) do not mention massicot in their more detailed analysis of these slags. At Zawar zinc–lead ores hosted in dolomite have been mined for centuries to recover zinc. The ore consists of galena and sphalerite plus chalcopyrite, arsenopyrite, pyrrhotite, argentite and cerussite. The ores were hand-sorted, roasted in air and then reduced in sealed clay bottles with coal to produce zinc vapour which condensed in the lower cooler parts of the furnace. Temperatures of 1000°C are required by this process. Friedlaender and Choo (1970) suggest that the massicot was formed by the roasting of galena but it is suggested here that it could also have been produced by the breakdown of the cerussite (PbCO$_3$). However the very small amounts of massicot produced by this process mean that it cannot be the manufacturing process of bint al dhahab.

At Agucha mine some 220 km north-north-east of Zawar, Craddock *et al.* (1989) describe the mining and benefication of silver-rich lead ores and the subsequent recovery of silver from the refined lead by the process of cupellation. Pliny (33.35) also describes the cupellation process used in Italy and goes on to describe (34.50) the use of the 'dross' of smelting as a traditional medicine. Cupellation consists of melting argentiferous lead in a shallow cupellation furnace and blowing air across the exposed surface at temperatures of 900–1000°C. The lead is oxidised to litharge which either blows

away or remains in the cupel from which it can be slagged off to produce large litharge cakes. The silver is recovered as a button which floats on top of the litharge. Litharge residues have also been found at Roman cupellation sites in the UK and Germany (Tylecote, 1990), indicating that use of this technique was widespread in the ancient world. Craddock *et al.* (1989) describe small clay cupellation vessels from the Agucha site with internal diameters of 25 to 30 mm. A plano-convex piece of litharge was also recovered which from its shape was caste in a larger vessel some 6 cms in diameter and 3 cms deep; about the same size as the many cupellation hollows discovered at Sardis in Turkey (Ramage, 1970, quoted in Craddock *et al.*, 1989). The curved shape of this fragment is very similar to the bint al dhahab described in this paper. The very low silver content of one of the specimens (Table 1) shows that this element was present in the primary material from which it was made. This together with the shape of the specimens is consistent with an origin of bint al dhahab by cupellation of argentiferous lead.

Traders in bint al dhahab in the souks of Oman say that the substance comes from Iran. There are many lead–zinc deposits in Iran, particularly in the central part of the country (Anon, 1992). The deposit closest to the Gulf coast lies about 150 km inland, some 100 km south-southeast of Shiraz. The abundance of lead deposits in Iran lends further weight to an Iranian origin for bint al dhahab. With regard to the origin of the modern supply, it is possible that either the material is being plundered from an ancient cupellation site or that the process is still being used today and bint al dhahab is being sold as a by-product.

Conclusions

X-ray diffraction and microprobe studies on bint al dhahab have confirmed that the substance is dominantly composed of lead oxide. However, the study has also revealed the presence of approximately 0.5 wt.% antimony oxide (SbO) and approximately 500 ppm of Cd and 300 ppm of As. Elements such as Fe, K and Al are also present in significant amounts. This information should help clinicians to devise more effective treatments for patients presenting with lead poisoning due to ingestion of bint al dhahab. The most likely origin for the bint al dhahab is cupellation, an ancient process used to recover silver from argentiferous lead by oxidising the lead in a blast of air to produce metallic silver and a litharge cake. The curved shape of the specimens and the presence of trace amounts of Ag are consistent with such an origin. The modern supply of bint al dhahab may be from the plundering of ancient sites or from an extant cupellation industry, possibly in Iran.

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Larnitic kirschsteinite from the Kotakonda kimberlite, Andhra Pradesh, India

N. V. Chalapathi Rao
S. J. B. Reed
D. M. Pyle
P. D. Beattie

*Department of Earth Sciences,
University of Cambridge,
Downing Street,
Cambridge, CB2 3EQ,
UK*

OLIVINES from igneous rocks generally have low calcium contents. However, olivines crystallized from strongly silica-undersaturated magmas occasionally contain large amounts of kirschsteinite (Ki: $CaFeSiO_4$) and monticellite (Mo: $CaMgSiO_4$) components. The purpose of this note is to report the first natural occurrence of kirschsteinite crystals that have larnite (La: Ca_2SiO_4) in the mineralogical norm.

These kirschsteinites are found as groundmass minerals within a kimberlite from Kotakonda in southern India. The compositions of the kirschsteinites in this rock range from $Mo_1Ki_{75}La_{24}$ to $Mo_{36}Ki_{61}La_3$, the molar Fe/(Fe+Mg) ratio of these crystals ranges from 0.63 to 0.99. Before these analyses, no larnite-normative olivines had been found in nature, and the most iron rich member of the Ki-Mo series was a magnesian kirschsteinite ($Ki_{69}Mo_{23}Fo_8$) reported from a melilite nephelinite (Sahama and Hytönen, 1957). The kirschsteinites found in meteorites all have a lower Ki content and are forsterite-normative (Dodd, 1971; Prinz et al., 1977).

The Kotakonda kimberlite (16°45′30″N; 77°38′30″E) is located about 50 km WNW of Mahbubnagar, in the state of Andhra Pradesh, India. It occurs as a 1.25 km-long E−W-trending dyke which intrudes biotite granites of Archaean age. The exposed rock is fresh and hard and constitutes the harde bank of the kimberlite. Crustal xenoliths of country rock are few while mantle xenoliths appear to be absent. A preliminary account of its geology was presented by Kameswara Rao and Sharma (1994).

Petrographic studies of thin sections of this kimberlite reveal the presence of two generations of forsteritic olivines − anhedral macrocrysts and the euhedral micro-phenocrysts, which are restricted to the groundmass. However, both types of forsteritic olivine are thoroughly serpentinised (Table 1). The