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Supplement of

A remarkable discovery of electrum on the island of Sylt, northern Germany, and its Scandinavian origin

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The gold and silver content - except six analyses provided by S. Nordrum - was determined by quantitative electron microprobe analysis. It was carried out using a Cameca electron microprobe (CAMECA SX 100) at the Mineralogical Institute, Universität Hamburg, Germany, operating in the wavelength-dispersion mode, with an accelerating voltage of 20 kV, a specimen current of 20 nA, and a beam diameter of approximately 1 µm. The standards used were Au 100 % (Au Lα) and Ag 100 % (Ag Lα).

Trace elements in our gold samples were analysed by LA-ICPMS at the Institute for Geosciences, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany, using a M50-E Resonetics 193 nm Excimer laser. Spot analyses were carried out on each sample using a 73 µm spot size and 10 Hz frequency. Energy density at the surface of the sample (i.e. fluence) was measured at 6-7 J/cm². The following nuclides were monitored: 53Cr, 55Mn, 57Fe, 59Co, 60Ni, 62Ni, 65Cu, 66Zn, 68Zn, 75As, 78Se, 105Pd, 107Ag, 108Pd, 109Ag, 111Cd, 118Sn, 195Sn, 120Sn, 121Sb, 123Sb, 125Te, 195Pt, 208Pb and 209Bi. All count rates were normalized to the internal standards 197Au or 57Fe. Normalized count rates were then converted to concentrations using measurements carried out on the external standards NIST SRM 610 (Jochum et al., 2011), and the PGE Ni7b sulfide reference material (Wohlgemuth-Ueberwasser et al., 2007), using the methodology described by Longerich et al. (1996). When more than one isotope for the same element was monitored, the relative natural abundance of each isotope was well reproduced, indicating that isobaric interferences were negligible. Ideally, a matrix matching external standard would be desirable to determine the trace element concentrations for these samples. Nevertheless, comparisons between the concentrations obtained using either NIST-SRM-610 or the PGE Ni7b sulfide as the external reference materials, yielded only minor variations (ca. 10 %). These results indicate that the ablation yields during laser emission were high enough to prevent significant elemental fractionation, in similar fashion to what was reported by Kamenetsky et al. (2013) in their measurements of the PGE and chalcophile element abundance of Pt-Sn-alloy saturated sulfide melt droplets.

Trace elements (53Cr, 55Mn, 57Fe, 59Co, 61Ni, 65Cu, 66Zn, 68Zn, 75As, 77Se, 108Pd, 109Ag, 111Cd, 118Sn, 119Sb, 123Sb, 125Te, 195Pt, 199Au, 208Pb, and 209Bi) in the Harnäs sample were analysed by LA-ICPMS at the Institute of Mineralogy, Leibniz Universität Hannover, Germany. A Spectra-Physics Solstice femto-second laser system based on a Ti:sapphire IR laser coupled to a Thermo-Scientific Element-XR fast-scanning sector-field-ICP-MS was employed. The laser optics shifted the wavelength into the UV spectra to 193 nm (for details, see e.g., Albrecht et al., 2014; Lazarov & Horn, 2015; Leissner et al., 2015). The sample and standards (NIST-610, PGE-A) were mounted in a self-made ablation cell controlled by a New Wave DUV stage system. The sample spot size was 20 µm, the ablation rate 2 Hz. The ablation cell was coupled to a Thermo-Scientific Element-XR fast-scanning sector-field-ICP-MS. All count rates were normalized to 100 %. PGE-A (a Ni sulfide doped standard with highly siderophile elements and other trace metals in the concentration range of 100 – 200 µg/g; Alard et al., 2000) was regularly run as an unknown sample for quality control.

Lead isotopes of three of our gold samples were determined at the Institute of Mineralogy, Leibniz Universität Hannover, Germany. From the Sylt sample, ~100 mg of electrum were scraped off with a thoroughly cleaned scalpel. The sample from the Kongsberg deposit was intergrown with quartz and calcite. To retrieve a sufficient amount of gold for Pb isotope analyses, ~6 g of sample material was crushed and ground to 200 to 500 µm in an agate mortar. The gold fraction was then separated from the matrix on a distributing jigger at a constant water flow, yielding ~1 g of a metal fraction. Remaining quartz and black grains (magnetite and/or amphibole?) in the metal fraction were removed by hand-picking under a
binocular. The sample from the Harnäs deposit was present mostly as gold with a minor occurrence of a brownish phase (probably Fe oxides). About 80 mg of material was used for analyses. Because the Pb concentration especially in the Sylt sample is low (< 5 µg/g, Table 3) and apparently not evenly distributed between core and rim, a potential contamination of anthropogenic Pb needs to be removed prior sample digestion by leaching. All gold fractions from all samples were leached in Savillex® teflon beakers in warm 3 M HCl for 30 min, followed by an additional step employing warm 7 M HCl for 15 min, and a final rinse step with 3 M HCl again.

During the first leaching step of the Harnäs sample, the acid turned deep yellow while the brownish phase was dissolving. We interpret this effect due to a breakdown of Fe oxides and formation of yellow Fe-Cl complexes. The possible high Fe content is additionally supported by our LA-ICP-MS data (Table 3, Fig. 6). After the final leaching step, a yellow color of the 3 M HCl was not discernible anymore. The other two samples (Sylt, Kongsberg) showed no coloring of the leach solutions. The unexpected high abundance of gold in the Kongsberg sample (Table 2) allowed to prepare three sample splits for replicate analyses. All leach solutions ("leachates") were dried, and the residues were kept for later Pb purification and isotope analyses. The cleaned gold fractions were then dissolved in aqua regia in closed teflon beakers at 130 °C over night. The solutions were subsequently dried down and the residues were treated three times with hot 6 M HCl (with intermittent drying steps) to re-mobilize Pb from the Au precipitates. Lead separation followed the method of Korkisch & Hazan (1965, see also Schuth et al., 2011), employing HBr (ultrapure grade, Roth, Germany) and HCl. The dry residues were covered with 0.5 M HBr, heated, dried, and covered with 1 mL 0.5 M HBr again. After transfer into centrifuge tubes and centrifugation at 4000 rpm, the samples and leachates were ready for Pb separation (see Schuth et al., 2011, for details). In addition, two procedural blanks, and an international reference material (BIR-1, basalt, USGS, USA) were analyzed. Of the BIR-1, ~100 mg powder was digested in concentrated HF-HNO₃ (5:1), after digestions it was treated as the gold samples. The purified Pb fractions were dissolved in 0.6 M HNO₃ for analyses. The Tl standard NBS-997 was added immediately prior analyses to the samples and standards for instrumental mass fractionation correction, yielding a Pb/Tl of 6 ±1.5 (Schuth et al., 2011). Analyses were performed with a Thermo-Scientific Neptune Plus multi collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS). The sample solutions were introduced into a Cetac Aridus-II desolvating unit equipped with PFA nebulizer (ESI, Germany) to improve signal intensity.

For interference correction of $^{204}$Hg on $^{204}$Pb, the $^{202}$Hg signal was measured, and a known $^{202}$Hg/$^{204}$Hg of 4.35037 was assumed. Mass bias correction was calculated employing the exponential law and a $^{203}$Tl/$^{205}$Tl of 0.418922 (Hg and Tl isotope ratios calculated from values from Berglund & Wieser, 2011). All Pb isotope ratios in this study are given relative to the NBS 981 triple-spike values reported by Galer & Abouchami (1998) with $^{206}$Pb/$^{204}$Pb = 16.9405 (±90 µg/g 2σ), $^{207}$Pb/$^{204}$Pb = 15.4963 (±103 µg/g 2σ), and $^{208}$Pb/$^{204}$Pb = 36.7219 (±120 µg/g 2σ). The Pb sample-to-blank ratio always exceeded 1,000. A blank correction was therefore not carried out. The results of the BIR-1 reference material were in perfect agreement with published data (Table 4).

References


