

SO225 – Gold-rich Manihiki magmas: A high precision LA-ICP-MS study of glasses obtained during SO193 and SO225 expeditions

Portnyagin M.V.¹, Golowin R.¹, Garbe-Schönberg D.², Hoernle K.¹, Werner R.¹, Hauff F.¹

¹ GEOMAR Helmholtz Center for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel

² Institute of Geosciences, Christian-Albrechts-University of Kiel, Ludewig-Meyn-Str. 10, 24118 Kiel

Association of continental flood basalts with gigantic sulphide deposits enriched in copper, nickel and platinum-group elements, such as in the Norilsk province (Russia), poses the question if submarine large igneous provinces also have large ore potential. In this work we used material obtained during R/V SONNE SO193 and SO225 expeditions to quantify the amount of chalcophile elements (Cu, Ag, Au) in parental magmas of the Manihiki Plateau and to elucidate their potential for the formation of sulphide deposits enriched in copper and precious metals.

Because low-temperature alteration processes can affect primary concentrations of chalcophile elements in bulk rocks, we focused this study on fresh volcanic glasses. These samples, rapidly quenched during submarine eruptions, circumvent post magmatic alteration and thus host primary information about melt compositions and provide a rare opportunity to quantify the amount of chalcophile elements in primary Manihiki melts. Seven samples studied belong to the low-Ti group ($\text{TiO}_2 < 0.5$ wt. %, Timm et al., 2011) of Manihiki Plateau basement lavas. They were collected from the flanks of deep troughs cutting through the plateau (Central Danger Island Trough: SO225-DR12 and SO193-DR26; Suvorov Trough: SO225-DR24). One sample representing high-Ti lavas ($\text{TiO}_2 > 0.5$ wt.%) comes from the northeastern flank of the Manihiki Plateau (SO193-DR52). Detailed geochemical description of Manihiki lavas can be found in papers by Timm et al. (2011) and Golowin et al. (this volume).

Chalcophile elements (Cu, Ag, Au) in the Manihiki glasses were analyzed by high precision laser-ablation inductively-coupled plasma mass-spectrometry (LA-ICP-MS) using an Agilent 7500s quadrupole mass-spectrometer

coupled with a 193 nm ArF excimer laser system Coherent GEOLAS Plus at the Institute of Geosciences of the Christian-Albrechts University of Kiel. A new analytical procedure especially designed for this study allowed us to quantify concentrations of Au and other chalcophile elements in glasses with long-term reproducibility better than 20% at concentrations above 0.001 ppm and the detection limit of 0.0002-0.0003 ppm which is about an order of magnitude lower compared to conventional techniques. A representative collection of mid-ocean ridge basalt (MORB) glasses and boninite glasses from Troodos (Cyprus) was analyzed along with the Manihiki glasses allowing their direct comparison.

Concentrations of Cu (95-97 ppm), Ag (0.020-0.038 ppm) and Ag/Cu ($2.1-3.9 \times 10^{-4}$) in low-Ti Manihiki glasses are within the N-MORB range (Jenner et al., 2012, our unpublished data) (Fig. 1a). High-Ti glass has distinctively high Cu (192 ppm) and Ag (0.057 ppm) concentrations and Ag/Cu (2.9×10^{-4}) similar to that in low-Ti glasses and N-MORB. Concentrations of Au in low-Ti glasses (0.0038-0.0052 ppm) and Au/Cu ($4.0-5.5 \times 10^{-5}$) are about 4 to 5 times higher than in N-MORB (Au < 0.001 ppm, Au/Cu < 1×10^{-5}) and primitive mantle (Fig. 1a). High-Ti glass also has high Au concentration (0.0052 ppm) but Au/Cu (2.2×10^{-5}) intermediate between those in MORB and low-Ti Manihiki glasses.

High Au content is unusual for oceanic magmas and requires specific process of magma origin or Au-rich source. Possible reasons for the Au enrichment in the Manihiki magmas are (1) entrapment of Earth core material in the plume source, (2) mantle melting in the presence of solid sulphide phase (monosulphide), and (3) very high degrees of mantle melting.

Moderately high Ni (82-192 ppm) and Ni/MgO (13-20 ppm/wt.%) in Manihiki glasses, similar to those in most primitive MORBs, make the involvement of the Ni-rich core material in their origin unlikely (e.g., Herzberg et al., 2013). The presence of solid sulphide in the source can be ruled out, because Manihiki magmas originated at high temperature (>1300 oC, Golowin et al., this volume) and have low Ag/Cu ratios incompatible with the element fractionation by monosulphide phase (Li and Audédat, 2013). More plausibly, the Au enrichment in the Manihiki glasses can be explained by extensive mantle melting (>25%) with sulphide being exhausted in the mantle residue. Under such conditions, Au begins to behave as a typical lithophile element, favoring the silicate melt during further mantle melting.

Indeed, the closest analogues of the Manihiki glasses are komatiites (Alexo, Canada; Gorgona Island) and boninites (Troodos, Cyprus) (Fig. 1a),

which are known to originate by more than 20% melting (e.g. Keays, 1995; Crawford, 1989). As illustrated by our modeling (Fig. 1a), high-Ti glass can originate from single stage equilibrium ~25% melting of a primitive mantle-like source followed by ~50% crystal fractionation. Low-Ti glasses have higher Au/Cu ratios than primitive mantle and komatiites and cannot be explained by single stage melting of primitive or slightly depleted mantle. A more plausible model for the origin of low-Ti Manihiki magmas as well as for Troodos boninites is second stage melting of a mantle source which experienced 15-20% melting during the first stage, resulting in significantly higher Au/Cu than in primitive mantle (Fig. 1). In the case of boninites, re-melting of previously depleted mantle is caused by a flux of water-rich fluids enriched in fluid-mobile elements (e.g. Pb, Fig. 1b). Manihiki glasses exhibit no Pb enrichment compared to MORB and primitive mantle. Therefore, their origin did not involve subduction fluid addition and is likely to be related to unusually high plume temperature and possibly to rifting during the Manihiki Plateau formation that facilitated further upwelling and re-melting of previously depleted plume mantle.

In conclusion, our data demonstrate unusual enrichment of Manihiki parental magmas in chalcophile elements and particularly in Au, which is related to very high degrees of single stage (high-Ti group) and two-stage (low-Ti group) mantle melting. The Manihiki magmas are undersaturated in sulphide at low pressure and therefore are unlikely to form magmatic sulphide deposits even after significant (up to 50%) degrees of fractionation. However, metamorphic transformation of these rocks can result in mobilization of chalcophile elements by fluids and formation of hydrothermal Au-mineralization by analogy with Archean komatiites (e.g. Keays, 1995).

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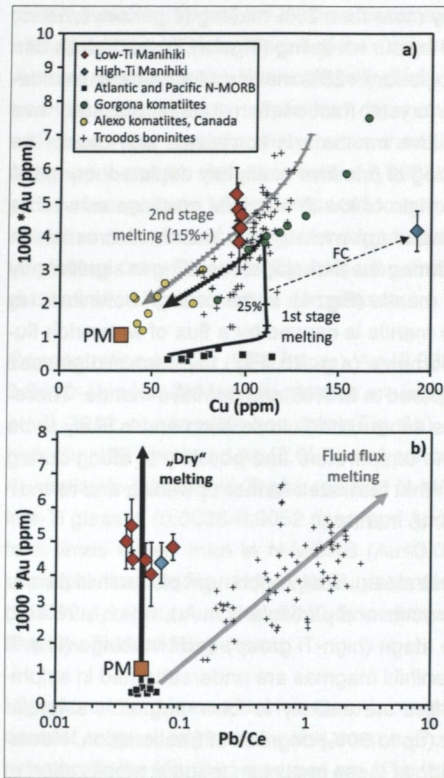


Figure 1. Systematics of chalcophile elements in Manihiki glasses. Composition of Manihiki glasses, Pacific and Atlantic N-MORB, and Troodos boninites from this study; Alexo and Gorgona komatiites from GEOROC database; primitive mantle (PM) after McDonough and Sun (1995). Modeling of 1st and 2nd stage (after 15% melt extraction of the 1st stage) is performed using model of Lee et al. (2012) for initial PM composition at $fO_2=QFM$, $T=1300$ oC and $P=2$ GPa. Dashed line shows trend of fractional crystallization (FC) for sulphide undersaturated system when Cu and Au behave as highly incompatible elements.