Mineralogy, geochemistry and age of greisen mineralization in the Li-Rb-Cs-Sn-W deposit Zinnwald, Erzgebirge, Germany

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The Erzgebirge (Krušné hory) is a world class area for Li-Rb-Cs-F-Sn-W-Bi greisen mineralization, which is associated to late-Variscan, postcollisional 'small intrusion' Li-F granites in space and time [1]. A typical example is the Zinnwald/Cínovec Li-Rb-Cs-Sn-W deposit, which is hosted by the Cínovec-Zinnwald granite cupola and Teplice rhyolite. Sn-W(-Li) mining was active for about 700 years until 1990. The exposed intrusion (1.3 x 0.3 km) is composed of a Li-F-granite which in part is strongly greisenized by high-temperature fluids [1, 2]. The flat dipping quartz-zinnwaldite-topaz-fluorite cassiterite greisen ore bodies in the German part of the Zinnwald deposit have a thickness of up to 25 m and resources of about 50 kt Li, 19.5 kt Rb, 1 kt Cs, 6.7 kt Sn, and 2.7 kt W [3]. Three representative zinnwaldite-rich quartz-Li-mica-topaz-fluorite-cassiterite greisen samples with a total weight of 30 t were taken in two levels of the old mining area. The average bulk geochemistry and the range of 16 greisen subsamples indicate the high concentrations of rare elements and fluorine: Li (3290, 490-6990 ppm); Rb (2320, 440-4900 ppm); Cs (67, 13-160 ppm); Sn (1620, 50-13.900 ppm); W (140, 25-390 ppm); Nb (90, 52-153 ppm); F (2.7, 0.36-4.3 wt.%); Th (38, 22-85 ppm). The geochemical signature (e.g., relatively high Li, Rb, Cs, F, Nb, Sn) of the greisen and Li-F granite show similar trends [1, 3]. Seven Li-mica separates have been dated by Ar-Ar in Freiberg (ALF) using laser step heating techniques and an ARGUS multicollector noble gas mass spectrometer. Ages are interpreted as near-formation ages of Li-mica and range between 312.6 ± 2.1 Ma and 314.9 ± 2.3 Ma (2σ external).

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Analysis of iodine, bromine and chlorine in marine sediments and carbonate nodules by ICP-MS

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Halogens are thought to be useful in the geochemical studies of rock and sediment formation. However, their analyses are difficult due to their low abundances, specifically Br and I. There are lack of reliable analytical results also for standard rocks. Therefore, we have examined separation procedures of Cl, Br and I from sediments and sedimentary rock samples by pyrohydrolysis. Halogens evaporated by pyrohydrolysis collected in trap solutions. The concentrations of Br and I were determined by ICP-MS and that of Cl was measured by ion-chromatograpy.

Using the developed methods, we have analysed Cl, Br and I in various standard rock samples. The analytical results agreed well with certified values. New data for standard rocks (e.g. JMS-1, JMS-2, JCp-1, JCt-1), in which the concentrations were not known, were also obtained.

We also analyzed sediments and carbonate nodules collected from methane hydrate areas in Japan Sea. In these areas, high iodine concentrations were observed in pore waters in the sediments. We also analysed Br and Cl for comparison.

Results obtained for these elements in solid phase of the sediments were in the ranges: Cl: 5000-10000 ppm, Br: 40-150 ppm, I: 10-200 ppm. High iodine concentrations are characterized by methane hydrate areas. Concentrations of Br and I showed the decreasing tendency with depth. Markedly high values of I in surface sediment was observed. This suggested that I was accumulated by the deposition of organic matters from seawater and also by the fixiation in oxic layer of the sediments from pore water. The concentrations of Cl, Br and I in carbonate nodules were about 100 ppm, 7 ppm, 4.6 ppm. I in carbonate nodules was found to be highly concentrated from pore water compared with Br. The I/Br ratios in carbonate nodules were much higher than those in pore water and solid phase of the sediments. Concentratian mechanisms of the iodine is being examined now.