Potentially hazardous trace elements in biomass burned in power plants

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The study is based on eight samples of biomass (OTR- corn bran; SLON-1 and SLON-2 – sunflower; TRO – sawdust; OLI – olive residue; SLOM - straw; BUK – beech bark; PAL – palm kernels) used in power plants in southern Poland and ashes obtained in relatively low temperature (475°C). Results are compared with average trace element contents in coal and coal ash [1].

Fourteen elements were selected as components of major environmental concern (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, Zn). Average values for hard coal are exceeded in biomass only for four elements (Table 1). The concentration of trace elements in biomass ash can be very high and for eight elements significantly exceed average values determined for coal ash (Table 2). The results indicate that concentration of several trace elements in biomass used as fuel and in biomass ash could be dangerous for environment.

Element	Average for hard coal	Highest values for studied biomass samples
Cd	0.2	0.31(TRO)
Cu	16	25 (OLI); 23 (PAL)
Mn	71	333 (PAL); 126 (OTR); 88 (BUK)
Zn	28	79 (OTR); 46 (PAL)

Table 1. Highest values of trace elements in biomass samples exceeding average value for hard coal (in ppm)

Element	Average for coal ash	Highest values for studied biomass ash samples
Ag	590	5319 (TRO)
Cd	1.2	71 (TRO); 2.1 (OTR); 1.66 (SLON-2)
Cu	110	587 (TRO); 509 (PAL); 266 (SLON-2); 255 (SLON-1); 178 (OTR); 169 (OLI)
Mn	430	>10 000 (TRO); 7373 (PAL); 2148 (OTR); 1507 (BUK); 444 (SLOM)
Mo	14	14.7 (OTR)
Ni	37	49 (PAL); 38 (OLI)
Pb	55	69 (TRO)
Zn	170	1923 (TRO); 1485 (OTR); 1051 (PAL); 428 (BUK); 399 (SLON-2); 321(SLON-1)

Table 2. Highest values of trace elements in biomass ash samples exceeding average value for hard coal ash (in ppm)

[1] Ketris & Yudovich (2009) *International Journal of Coal Geology* **78**, 135-148.

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Synchysite: Implications for Titanite Destabilisation and Differential REE, Y and Th Mobility in the Soultz Monzogranite

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High heat-producing granitic rocks (HHPGs) are characterised by abnormally enriched values of radiogenic U, Th and K above upper continental crustal averages. In recent years, HHPGs have received considerable attention as they can be targeted for enhanced geothermal systems (EGS). The Soultz-sous-Forêts monzogranite is a notable example. With the exception of K, U and Th commonly occur with rare earth elements and yttrium (REE and Y, REY) in primary accessory phases [1]. Upon interaction with hydrothermal fluids, accessory phases such as titanite, may destabilise and form polymineralic metasomatic assemblages. Analysis of these metasomatic minerals is integral for understanding not only the chemistry of the hydrothermal fluid, but also the mobility of elements previously held in primary accessory phases. As such, this study focuses on the comparative EPMA of primary and metasomatic accessory phases to further the understanding of REE, Y and Th mobility in the Soultz monzogranite.

Petrographic studies show primary REY and Th-bearing titanites have been altered to anatase + calcite + quartz + synchysite-(Ce) $[(Ce,Ca,Th)(CO_3)_2F]$ ± bastnaesite-(Ce) $[(Ce,Th)(CO_3)F]$ or monazite-(Ce) $[(Ce,Th)PO_4]$ + xenotime-(Y) $[(Y)PO_4]$ ± thorite $[ThSiO_4]$. These observations represent the first documented citing of synchysite-(Ce) formation through titanite destabilisation. The purely fluorocarbonate-bearing assemblage is restricted to samples exhibiting minor selective alteration. Phosphate-bearing assemblages are, however, found in pervasively altered samples where primary apatite was significantly affected. Comparative mass balance studies of titanite, synchysite-(Ce) and monazite-(Ce) found $HREE_2O_3$, Y_2O_3 and ThO_2 levels to be relatively depleted in fluorocarbonate-bearing samples. Although ThO_2 levels were maintained in monazite-(Ce) relative to parent titanite, $HREE_2O_3$ and Y_2O_3 appeared lower due to the presence of xenotime.

Following the experimental work of Hunt and Kerrick [2], the ingress of CO_2-rich fluid was integral for titanite destabilisation. On the other hand, fluorine in synchysite was most likely sourced from proximal chloritised biotite. Following synchysite formation, excess FCO_3^- or HCO_3^- anions may have remained in solution and led to the significant mobilisation of HREE, Y and Th through complexation. Our study provides evidence for not only differential REE and Y mobility in the Soultz monzogranite, but also that Th, conventionally considered an immobile element, is mobilised under certain hydrothermal conditions.

[1] Bea (1996) *J Petrol* **37**, 521-552. [2] Hunt & Kerrick (1977) *Geochim Cosmochim Ac* **41**, 279-288