

Trace elements and lead isotopes in moldavites: Source material fractionation or variable parent lithologies mixing?

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Samples and data collection

Contents of selected minor and trace elements and lead isotope composition have been determined for 16 moldavites from South Bohemian (4), West Moravian (5) and Cheb Basin (7) partial strewn fields. Data were measured using ICP-MS technique from solution following the protocol of Strnad *et al.* [1].

Results

After normalizing the measured values to average element contents for moldavites from the South Bohemian partial field it appeared that the moldavites from Cheb Basin differ from those from South Bohemia and Moravia. They are highly enriched in Zn, Ba, Pb, and U while they display significant depletion in Cr and Ni. Moravian moldavites display either no or significantly less differences when compared to South Bohemian moldavites.

Chondrite-normalized REE contents overlap existing literature data. HREE tend to be enriched in Moravian samples whereas the samples from the Cheb Basin appear to be depleted in HREE compared to the moldavites from the South Bohemian field. Concentrations of LREE remain more or less invariant among all regions.

In the plot $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ the moldavites from the Cheb Basin are clearly separated from the rest of the samples analyzed; samples from South Bohemia and Moravia do not differ.

Conclusions

The data collected do not corroborate idea of selective source material fractional vaporization, or that of selective condensation neither the hypothesis of Engelhardt *et al.* [2] explaining the formation of moldavites by preferential trapping of large ions into early condensates. We assume that measured composition reflects the lithological variability of the target area instead.

[1] Strnad *et al.* (2005) *GGR* **29**, 303–314. [2] Engelhardt von W. (2005) *GCA* **69**, 5611–5626.

Nitrogen isotope fractionation during the oxidation of substituted anilines by manganese oxide

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Primary aromatic amino groups are often the position of initial attack during the mineral-catalyzed oxidative transformation processes of soil and groundwater contaminants. Here, we explored the N isotope fractionation associated with the oxidation of substituted anilines as a diagnostic tool for identifying the initial oxidation steps of such degradation processes. Apparent ^{15}N -kinetic isotope effects, AKIE_N , were determined for oxidation of various substituted anilines in suspension of manganese oxide (MnO_2) and compared to reference oxidation experiments in homogeneous solution and at electrode surfaces, as well as to density functional theory calculations of intrinsic KIE_N for electron and hydrogen atom transfer reactions.

Spectroscopic characterization of MnO_2 -particles as well as the investigation of co-solute effects on mineral reactivity showed that despite complex reaction kinetics of contaminant disappearance, substituted aniline oxidation occurred in one elementary, isotope-sensitive reaction step. Owing to the partial aromatic imine formation after one- electron oxidation and corresponding increase in C–N bond strength, AKIE_N -values were *inverse*, substituent-dependent, and confined to the range between 0.992 and 0.999 in agreement with theory. However, AKIE_N -values became *normal* once the fraction of cationic species prevailed owing to ^{15}N -equilibrium isotope effects, EIE_N , of 1.02 associated with N atom deprotonation. The observable AKIE_N -values are substantially modulated by the acid/base pre-equilibria of the substituted anilines and isotope fractionation may even vanish under conditions where normal EIE_N and inverse AKIE_N cancel each other out. Our work suggests that the observed pH- and substituent-dependent trends of N isotope fractionation provide a new line of evidence for the identification of oxidative degradation processes of substituted primary aromatic amines.