

Nitrogen isotope systematics and origins of mixed-habit diamonds

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Mixed-habit diamonds form when growth occurs by two different simultaneous growth mechanisms [1, 2]. The two crystal habits are smooth, flat {111} crystal faces (octahedral growth) and curved, hummocky, non-faceted surfaces with a mean orientation of {100}, but this can be inclined by up to 30° (cuboid growth). This type of growth can produce a range of centre-cross or star-shaped patterns within the diamond [3], which are the result of light-scattering defects that occur only in the cuboid sectors. When these defects are graphitized and thus opaque, the cuboid growth sectors appear much darker than the gem-quality octahedral sectors.

Analysis of this type of diamond has shown that carbon isotopes show no partitioning between growth sectors [4]. However, nitrogen contents are much higher in the octahedral sectors (enriched by up to 160% compared with that of cuboid sectors), while nickel and cobalt are partitioned into the cuboid sectors if available in the diamond-forming fluid [5]. Few nitrogen isotope data exist for these types of diamonds. One study showed no N-isotope fractionation between growth sectors [6] but the sample used in that study is not thought to be a true mixed-habit diamond.

This study compares nitrogen-isotope data obtained via SIMS and by step-wise oxidation mass spectrometry from both octahedral and cuboid growth sectors, with the goal of investigating both isotopic fractionation and the source of nitrogen in these unusually N-rich diamonds.

[1] Frank (1967) *Proc. Int. Industrial Diamond Conf.*, 119-135. [2] Lang (1974) *Proc. R. Soc. Lond.*, **A. 340**, 233-248, [3] Welbourn *et al* (1989) *J. Crystal Growth*, **94**, 229-252, [4] Howell *et al* (2013) *Am. Min.*, **98**, 66-77, [5] Howell *et al* (in press), *Chem. Geol.*, [6] Cartigny *et al* (2003), *Geochim. Cosmochim. Acta*, **67**, 1571-1576.

Sorption behavior of lithium

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Salar the Uyuni is one of the greatest sources for Li being presently assessed. It is not yet understood why one observes great Li enrichment in the delta areas of past and presently inflowing rivers. One theory is temporary sorption and subsequent desorption by clay minerals that are enriched in these inflow areas.

Li sorption on clay minerals, namely kaolinite and bentonite, and on clinoptilolite, a zeolite, was studied in batch experiments with subsequent ICP-MS analysis. Solid/solution ratio was 1:4; shaking time was 24 hours; pH was varied between 2 and 10, with focus on pH 6 and 8 as pH in the Salar is circum-neutral. Li concentration in the solutions was varied between 1.5 and 750 mM; sodium concentration between 0.01 and 5 M.

It was found that Li was sorbed by all minerals; highest sorption being achieved at lowest sodium and highest Li concentration for clinoptilolite (3890 ppm) and bentonite (3820 ppm); at 3 M Na and highest Li concentration for kaolinite (1250 ppm). Absolute Li sorption at pH 6 and 8 was similar and increased with increasing Li concentration in the initial solution at constant Na concentration. Relative Li sorption decreased due to limited exchange sites on the mineral's surface. At constant Li concentration, increasing Na caused Li sorption decreased by competition.

pH changes altered minerals' surface charge by (de)protonation, caused structural changes, or decomposition. For bentonite and clinoptilolite, pH-dependent sorption results scattered. The reason for that is not known. For kaolinite sorption was maximal at pH 2-4 which could be explained by surface complexation or incorporation in the crystal structure. Above pH 5, kaolinite probably transformed to gibbsite with effects on surface charge and on Li sorption.

This study showed that clay minerals and zeolites are effective Li sorbents and may contribute to elevated Li concentration at the freshwater inflows of Salar de Uyuni.