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Boron isotope fractionation in pegmatite systems: the role of aluminoborosilicate compounds in melts and aqueous fluids

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Boron has no natural redox chemistry. Fractionation between the two isotopes (^{10}B and ^{11}B) is almost entirely controlled by their relative partitioning between trigonal (BO_3, $B(OH)_3$) and tetrahedral (BO_4, $B(OH)_4^-$) species: ^{11}B with its lower vibrational energy is preferentially partitioned into the high ionic potential trigonal species, whereas the higher vibrational energy of ^{10}B favours uptake into the lower ionic potential tetrahedral species. The large mass difference between the two isotopes produces a significant range of isotope composition in nature (δ^{11}B from ca. +60 to -30 ‰). In spite of the increasingly application of boron isotopes as a tracer in petrologic, planetary, ore deposit and environmental studies our knowledge of the isotope fractionation factors remains poor. In particular, few experimentally determined boron isotope fractionation factors are available and theoretical semi-empirical values are widely used in the literature. Moreover, many studies on natural rocks and fluids have shown systematic downward offsets of δ^{11}B values from the theoretical curves that have been recently confirmed by ab-initio studies. The latter studies have also indicated that the four-coordinated BO_4 bonding (or vibration) in silicate minerals is substantially different from that in $B(OH)_4^-$ in a fluid. Thus, fractionation data for $B(OH)_4^-$ cannot be applied to BO_4 tetrahedral groups in minerals and melts, and boron isotopic fractionation occurs during both trigonal-tetrahedral and tetrahedral(fluid)-tetrahedral(mineral) exchange.

A similar behaviour is expected during trigonal(fluid)-trigonal(mineral) isotope exchange as already pointed out by few experimental studies performed on tourmalines synthetised from aqueous fluids containing trigonal boron.

The isotope fractionation factors between trigonal boron in fluids and tourmalines determined in experimental studies is in contrast with the quite homogeneous boron isotopic compositions measured in natural tourmalines crystallised in some pegmatitic systems from Elba Island (Italy) and Madagascar. The apparent discrepancies among synthetic and natural systems can be explained by the existence, in natural melts and aqueous fluids, of alumino-borate and boroaluminosilicate clusters and networks that can be incorporated in the mineral structure with negligible isotopic fractionation.