

SOA formation via aqueous reactions of phenols from wood combustion

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Introduction

While secondary organic aerosol (SOA) is generally considered to arise from the gas-phase oxidation of volatile organics, recent work has shown that aqueous-phase reactions can also form low volatility products that remain in the particulate phase after drop evaporation. This aqueous formation of SOA has been shown to be important for molecules such as small carbonyls, and other work has suggested that phenols might also be important. Large amounts of gaseous phenols are emitted from wood combustion, but little is known about the kinetics of phenol oxidation in the aqueous phase or about SOA yields.

In this project we examined the kinetics and SOA yields of three representative phenols in aqueous solution: phenol, 2-methoxyphenol (guaiacol), and 2,6-dimethoxyphenol (syringol). We examined the transformation of each compound in the dark, with simulated sunlight, and with a combination of simulated sunlight and OH (formed via photolysis of hydrogen peroxide).

Results

All three of the phenols are degraded in the presence of OH and/or light to form SOA; no phenolic loss or SOA formation was observed in the dark. Lifetimes of the aqueous phenols with respect to reaction with OH (and light) under atmospheric conditions are on the order of a few hours (syringol and guaiacol) to a few days (phenol). For guaiacol and syringol, most of this decay is due to direct photoreaction, while for phenol it is all due to OH reaction. In contrast to this wide range of kinetic reactivities, all three of the phenolic compounds very efficiently formed SOA. At pH 5, the SOA yields (defined as mass of SOA formed per mass of phenol reacted) ranged between 1.0 - 1.5 for all three compounds. The SOA yields at pH 7 were somewhat lower, 0.7 - 1.2, but still close to unity. These exceptionally high SOA yields, combined with the fast kinetic reactivity and large emissions, suggest that phenolic compounds from wood combustion are a significant source of SOA via aqueous-phase reactions.

Lu-Hf dating of metamorphism

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Lu-Hf garnet geochronology potentially offers an excellent tool for dating metamorphism. Advanced mineral separation and chemical sample pre-treatment, despite some problems (e.g. chemically induced parent/daughter fractionation) proved to be very helpful in recovering the *true* isotopic ratios of the analysed minerals and helped to achieve high age precision. While achieving high precision is not particularly difficult, the meaning of the obtained ages can be problematic even for garnet, commonly assumed to be relatively easy for linking its age with metamorphic conditions. Inheritance, multiple and prolonged growth or involvement in the retrograde reactions influence accuracy of garnet ages. However, *in situ* trace elements studies along with careful petrography and high spatial resolution dating help to provide not only better age interpretation but also information on rates and duration of metamorphism.

Separate core and rim dating of a garnet crystal from high grade gneisses from the Broken Hill area showed that, at least in some geological settings, garnet may grow for as long as 15 Ma. Such long growth has important consequences for, the most commonly applied, bulk garnet dating technique. High precision growth ages obtained for bulk garnet do not take into account the prolonged crystallisation time and thus underestimate age uncertainty. Another consequence of applying bulk garnet dating technique to such slowly crystallizing garnets is that mixing different proportions of older cores with younger rims will result in higher scatter of data points in isochron diagram, lowering age quality or even in preventing obtaining a well defined date.

Garnet dating may be biased already at mineral preparation stage. In the case of eclogites from the Sanbagawa belt, cleaner cores were picked preferentially to inclusions rich rims, which resulted in an age c.25 Ma older than accepted time of eclogite facies metamorphism. Petrographical and trace element studies proved that the obtained age represents, earlier, epidote amphibolite facies, garnet growth phase represented by much cleaner garnet core.

Whereas trace elements studies were very successful in explaining the Lu-Hf ages in the Sanbagawa belt, they appeared insufficient in explaining age inconsistencies in more complex polymetamorphic rocks of the Scottish Highlands.