Synthesis of Mn minerals at ambient temperature and pressure

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Manganese minerals are widespread in soils, sediments, water and ores. Particularly, Mn oxides play important roles in many soil chemical processes, are effective sorbents for metal ions and can oxidize organic and inorganic contaminants. Manganese oxides mostly occur together with other minerals and are therefore difficult to separate. To study fundamental processes on reactivity and kinetics pure phases are needed.

The objective of this work was to synthesize Mn minerals at ambient conditions and without the use of strong acids and bases. We designed 4 different experimental approaches based on $KMnO_4$ reduction. The reaction time varied between 1 and 550 days and the influence of the organic modificators acetate, citrate and lactate was checked. The reaction products were characterized mineralogically (XRD, FTIR), morphologically (SEM, BET) and chemically (SEM-EDX, ICP-OES, IC).

After a period of 1 day a poorly crystalline precursor birnessite [$K_4Mn_{14}O_{27}\bullet 9H_2O$] was the sole mineral phase that was formed in all reaction batches. Depending on the educts and on the modificator, several transformations of birnessite were observed over time. In 3 of 4 experiments without modificator, birnessite remained stable but increased in crystallinity and decreased in surface area with time. In one approach birnessite was stable in the first 90 days followed by slow dehydration and transformation to cryptomelane [KMn_8O_{16}].

The modificator acetate showed no effects on both crystallization behavior and mineral transformation. Birnessite that was formed in the presence of either citrate and sulfate, or citrate and chloride partly transformed to rhodochrosite [$MnCO_3$]. Chloride especially promoted this carbonization, which ended after 185 days in an equilibrium state. The final precipitate contained 80% rhodochrosite and 20% birnessite. Citrate had no effects on the reaction in the other 2 approaches and birnessite remained stable. Also lactate promotes the formation of rhodochrosite in the presence of sulfate or chloride. In contrast to citrate, lactate transformed the residual birnessite to manganite [γ-MnOOH]. In the other 2 approaches lactate induced a complete transformation of the precursor birnessite to feitknechtite [β-MnOOH] between 7 and 30 days after starting. The lactate- induced transformation of birnessite to manganite or feitknechtite could be related to the strong reducing property of lactate.

Our pathways to synthesize Mn minerals are feasible on a large scale, can produce crystallites in different sizes and with a well-defined surface area. The products can serve as model minerals in studies on kinetics and reaction behaviors of Mn minerals, and may also have a potential for remediation of contaminated sites.

Magmatic degassing in contrasting volcanic systems of the Vanuatu arc: constraints from uranium-series isotopes

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Recent and present volcanism in the Vanuatu arc (South West Pacific Ocean) occurs at a variety of volcano types that exhibit a wide range of eruptive behaviour: from post-caldera lava-lake activity and lava flows at shield volcanoes (Ambrym), moderately explosive sub-plinian events and associated pyroclastic-flows and lava flows at stratovolcanoes (Lopevi), to persistent strombolian and vulcanian-style eruptions at scoria cones (Yasur). This precludes a generic model of magmatic and eruptive behaviour for the Vantuatu arc volcanoes and necessitates a detailed study of each system.

Uranium-series disequilibria in volcanic rocks offer unique insights into pre-eruptive magmatic systems over process-relevant timescales e.g., ^{238}U-^{230}Th (380 Ka), ^{230}Th-^{226}Ra (8 Ka) and ^{226}Ra-^{210}Pb (100 a). The short half-life of ^{210}Pb ($t_{1/2}$ = 22.6 years) and the volatile nature of the intermediate isotope, ^{222}Rn, (intermediate between the ^{226}Ra parent and ^{210}Pb daughter) provide valuable information on magma transport, evolution and degassing over a timescale more pertinent to the processes leading up to volcanic eruptions.

We present new Uranium-series isotope data (U-Th-Ra-^{210}Pb) for young (< 100 years old) volcanic samples from Ambrym, Lopevi and Yasur volcanoes to investigate the timescales of magmatic evolution and degassing in the contrasting volcanic systems. ^{210}Pb deficits ((^{210}Pb/^{226}Ra)$_0$ < 1) in Ambrym and Yasur volcanic rocks suggest effective open-system magmatic degassing of ^{222}Rn, consistent with the persistent lava-lakes/exposed magma and significant gas emissions observed at both volcanoes. Lopevi, on the other hand, displays excess ^{210}Pb ((^{210}Pb/^{226}Ra)$_0$ > 1) in the most mafic samples suggesting that ^{222}Rn gas accumulation and fluxing preceding and/or during eruption (on a decadal timescale) may be responsible for the more explosive-style of eruption witnessed at this volcano. Significant accumulation of recently crystallised plagioclase phenocrysts can also create ^{210}Pb excesses in volcanic rocks, however, this process is not supported by the petrographic and geochemical data. In summary ^{210}Pb-^{226}Ra disequilibria in Vanuatu volcanic rocks reveal a strong link between pre-eruptive magma degassing systematics and the resultant style of volcanic activity.