Iodide and iodate interactions with clay minerals

ANDREW MILLER[1*], JESSICA KRUICHAK[1], HERNESTO TELLEZ[1], YIFENG WANG[1]

[1]Sandia National Laboratories, Albuquerque, USA, andmill@sandia.gov (* presenting author)

Abstract

Clay minerals are likely candidates to aid in waste isolation due to their low permeability, favorable swelling properties, and high cation sorption capacities. Iodine-129 is often the major driver of exposure risk from nuclear waste repositories at timescales >10,000 years. Therefore, understanding the geochemical cycling of iodine in clays is critical in developing defensible quantitative descriptions of nuclear waste disposal.

Anions are not typically considered to interact with most clays as it is assumed that the fixed negative charge of clays actively repels the dissoloved anion. This is corroborated by many batch studies, but diffusion experiments in compacted clays have shown iodide retardation relative to chloride. The reasons for this are unknown; however, several possible hypotheses include: redox transformation controls on sorption behavior, complex surface charge environments due to overlapping charge domains, and sorption to ancillary minerals or weathering products.

A series of clay minerals have been examined using several techniques to chracterize the surface charge environment of the clays, as well as to discern the potential for redox transformation and variable sorption behavior of different iodine oxidation states. Surface charge environments were examined through surface titrations and cation exchange capacity determination with methylene blue. Batch sorption experiments were completed with illite and palygorskite samples with both iodide and iodate. The batch experiments were completed at a range of pH values from 4-10, and at a constant ionic strength of 0.1M NaCl. Sorption experiments were performed at 20g/L solid:solution ratios to exacerbate sorption properties. The results show a range of sorption behaviors based on the clay mineral involved, as well as chemical conditions such as pH. Palygorskite has a higher sorption affinity for iodide compared to illite. There is evidence for some anion exhchange capacity on palygorskite; iodide sorption led to fluoride release. While not typically considered as a disposal medium, this result points to the use of alternative clay minerals to further isolate anionic components in nuclear waste.

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Peach Spring Tuff, Arizona-California-Nevada, USA: Generating an isolated supereruption

C.F. MILLER[1*], A.S. PAMUKCU[1], C.A. FERGUSON,[2] , T.L. CARLEY[1], G.A.R. GUALDA[1], J.L. WOODEN[3], W.C. MCINTOSH[4], M. LIDZBARSKI[5], J.S. MILLER[5], AND S.M. MCDOWELL[1]

[1]Vanderbilt Univ, Earth & Env Sciences, Nashville USA, calvin.miller@vanderbilt.edu (* presenting author)
[2]Arizona Geological Survey, Tucson USA, caf@email.arizona.edu
[3]Stanford U, Geol & Env Sci, Stanford USA, jwooden@stanford.edu
[4]NM Tech, Earth & Env Sci, Socorro USA mcintosh@nmt.edu
[5]San Jose State Univ, Geology, marshalidz@aol.com

The >700 km^3 Peach Spring Tuff (PST) is exposed through much of the western Colorado Plateau and the extended terrane of southern Nevada, SE California, and NW Arizona. Voluminous early volcanism and plutonism characterized the early Miocene history of this region, but large ignimbrites were rare and PST was almost an order of magnitude larger than any other erupted deposit.

Discovery of the source of PST (Silver Creek caldera, southern Black Mtns, AZ [Ferguson 2008]), a refined ^{40}Ar/^{39}Ar sanidine age (18.78±0.02 Ma, intracaldera & outflow [Ferguson et al in rev]), and detailed studies of pumice [Pamukcu et al in revision] shed light on the eruption and magma chamber evolution that preceded it. Phenocryst assemblages are consistently san>plag+bio+ hbl>qtz+px, +prominent sphene+zrc+all/chev. However, intracaldera pumice is distinct from distal outflow: richer in phenocrysts (~30-40%, showing strong resorption textures, vs $\leq$10%, mostly euhedral), trachyte rather than rhyolite (66-69 wt% SiO_2 vs 74-76 wt%). Thick proximal sections have common high-Si pumice, but in their upper parts crystal-rich, low-Si rhyolite-trachyte pumice is present. Core-rim zoning in zrc and sph in lower-Si pumice have compositions suggesting late growth from hotter less evolved melt (e.g. zrc rims to 50 ppm Ti: T>~900 C), in contrast to normally-zoned counterparts in high-Si pumice. Crystal size distributions and resorption textures also point to late heating in low-Si but not high-Si pumice.

We propose that trachyte in the caldera and proximal outflow represents basal cumulate mush within a zoned magma body, and that Si-rich outflow pumice was derived from higher levels. Only the lower portion was affected intensely by a pre-eruption heating event. Rhyolite-MELTS simulations suggest that the trachyte was melt-poor and ineruptible prior to reheating. The most plausible mechanism for heating and destabilizing of the mush, and perhaps for triggering eruption as well, is basal injection of hot, more mafic magma. Mafic injection is consistent with presence of sparse andesite magmatic enclaves within the ignimbrite and of a near-caldera basaltic andesite lava that was was emplaced just prior to the PST supereruption.

Regional uniqueness of the PST poses a conundrum: either super-quantities of eruptible magma or triggers to destabilize them must have been generally lacking, yet regional magma flux was high and interaction between felsic and mafic magma was ubiquitous.