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Forming an economic bentonite resource in a volcanic arc environment: Milos island, Greece

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Volcanoes in island arcs can undergo edifice evolution that includes submarine and subaerial volcanism, providing a dynamic environment of magmatic heat and volatiles that drives hydrothermal fluid flow with potential inputs from sea and/or meteoric water. This, in turn, can generate significant hydrothermal alteration that can result in economic deposits of industrial minerals. One example includes bentonite, a smectitic rock composed dominantly of montmorillonite.

Economically viable bentonite deposits are typically only 0.5 – 5 meters thick and although Wyoming-type bentonites comprise 70% of the world's known deposits, they are commonly no thicker than 8 m. The island of Milos is Europe's largest and actively mined calcium bentonite resource from volcanic piles exceeding 80 m thickness. Here, we use the Milos island example to understand how magmatism, volcanic edifice evolution and hydrothermal activity interact. We integrate field relationships of volcanic stratigraphy and alteration zones, with clay mineralogy (XRD), stable (S, O and H) isotope analysis and high precision geochronology (CA-ID-TIMS zircon U-Pb, and alunite Ar-Ar) to elucidate the timescales, thermal drivers and fluid components that lead to the development of a globally important bentonite resource.

A vertical transect through bentonite-altered volcanic stratigraphy indicates multiple magmatic pulses ca. 2.8 Ma with a submarine andesitic cryptodome and accompanying pepperitic hyaloclastite. Cumulative volcanic and sub-volcanic processes occurred over ca. 170 kyrs, resulting in a vertically and laterally extensive volcanic pile overlain by an episode of magmatic quiescence and brackish-water diatomaceous sediments. It is overlain by a silicic pyroclastic flow host to pervasive silica-alunite-kaolinite alteration. Stable isotopic analyses of bentonite indicate a hydrothermal origin at around 70°C with the fluid being sourced from sea and meteoric waters. The timing of formation is defined by a maximum duration of ca. 170 kyrs, with clear geological evidence that a significant period of alteration occurred within < 20 kyrs at ~ 2.64 Ma. Alunite sulfur isotope compositions reflect steaming ground activity that could be interpreted as the oxidised, shallower level counterpart to a boiling geothermal system linked to development of

extensive bentonite. However, the timing of alunite can be clearly resolved to > 1.5 myrs after bentonite formation to ~ 1.0 Ma, supporting a later overprint origin due to relatively recent steam heating of groundwater after emergence of the submarine system.

This study identifies key parameters that have resulted in the formation of an economic-scale bentonite resource on the emergent island of Milos. We conclude that the hydrology needed to form a bentonite deposit is not constrained to the marine environment and can be connected to emergent parts of the volcanic edifice. High precision geochronology indicates bentonite development happens on volcanic timescales (10 to 100 kyrs). A cumulative volcanic and sub-volcanic pile coeval with the formation of bentonite suggests multiple magmatic episodes over narrow timeframes provide and sustain the thermal driver for significant bentonite development. After emergence and development of a groundwater system, the subsequent steam heating is deleterious to grade and results in the development of alunite-kaolinite overburden.