



Serpentine Dehydration and the Mobility of Europium

Scott A. Wipperfurth*, Dr. Phillip D. Ihinger*, and Dr. Jill W. Ferguson*

University of Wisconsin-Eau Claire, Eau Claire, WI 54702

*Department of Geology; *formerly Materials Science Center, Now at: Interfacial Solutions, River Falls, WI

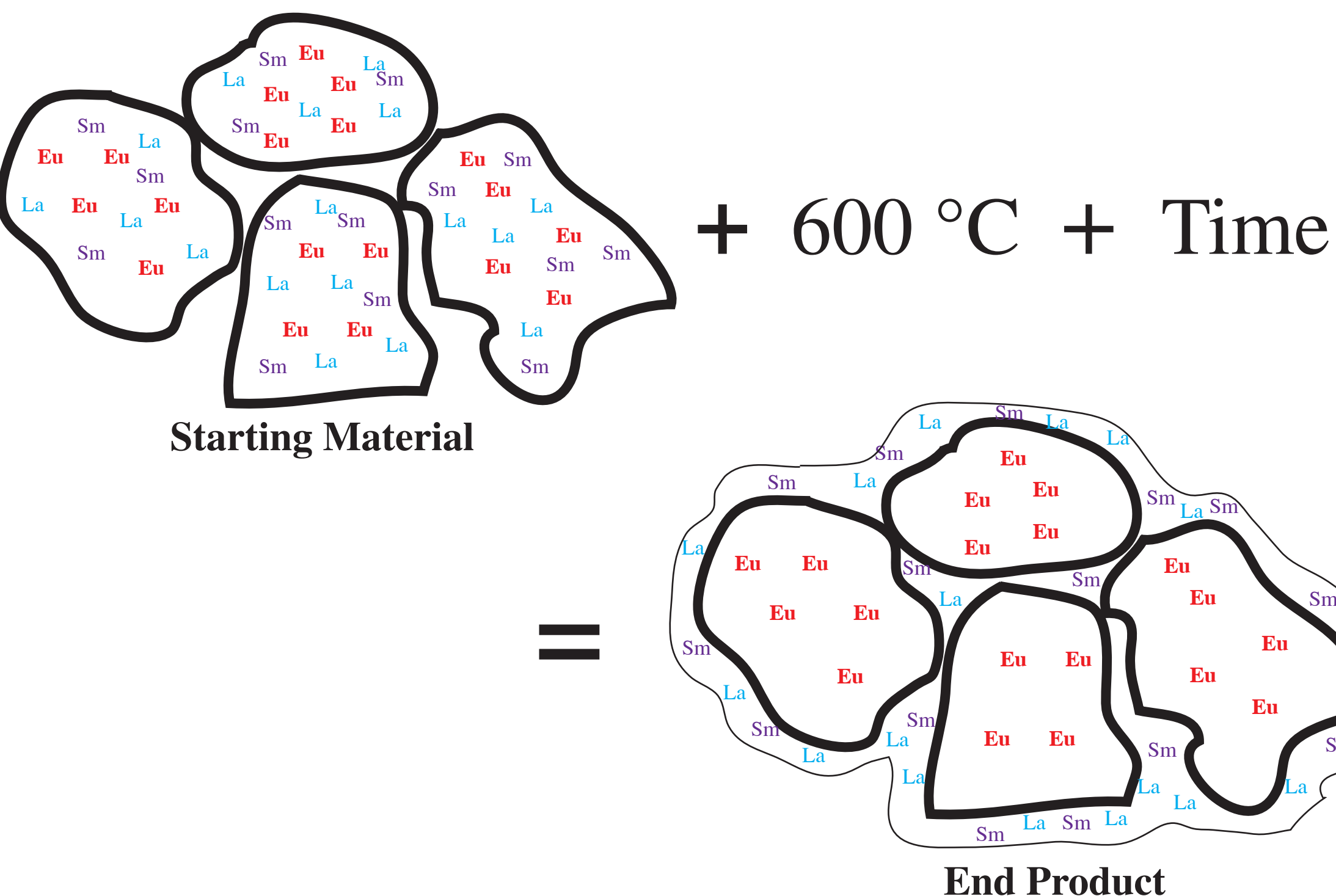
Abstract

Two distinct styles of continental crust formation, correlative in time, have been identified in the literature (Taylor and McLennan, 1995). However, much is still unknown about the mechanisms for generating new continental crust and why they shifted in Earth history. Continental crust created after 2.6 Ga in subduction arcs displays a prominent negative europium anomaly compared to the element budget of its mantle source. Intra-crustal differentiation with subsequent delamination of a lower Eu-enriched eclogitic crust has been proposed as a mechanism for the Eu depletion observed in upper continental crust, but concerns related to rock mechanics in the rigid lithosphere have yet to be satisfactorily addressed. We hypothesize that the complementary Eu enrichment is to be found in the dehydration residue of subducting slabs, which offers a well-known mechanism for recycling fractionated material back into the underlying mantle. We present exploratory experiments that investigate the nature of Eu mobility during the dehydration of oceanic crust. Serpentine, the dominant rock type found in sinking slabs, was collected from the Franciscan Complex of northern California. Starting materials were powdered and loaded in 1 atm tube-furnaces and held at temperatures between 500 and 600 °C for run durations varying from days to weeks. Run products were analyzed with XRD for phase identification and ICP-MS for REE abundances.

Hypothesis and Methods

We hypothesize that the complementary reservoir to the Eu-depleted continental crust can be found in the melting products of recycled oceanic crust: ocean island basalts in the oceanic setting and kimberlites and lamprophyres in the continental setting. Our hypothesis is based on initial observations of an Eu enrichment in alkaline rocks of the New England Lamprophyre suite (Boer et al., 2008). Europium's ability to inhabit a 2+ state, apart from the 3+ nature of other Rare Earth Elements (REEs), allows it to replace other 2+ ions in crystal lattices. Eu²⁺ is hypothesized to replace Ca in the aluminum-rich phase (feldspar/garnet) within the subducting slab and thus remains within the subducting slab while the other REEs are transported away within fluids generated by the dehydration of serpentine. This process is analogous to the process that generates the negative Nb and Ta anomaly in arc magmas. The trapping of Eu within the subducting slab causes the characteristic negative Eu anomaly observed within the modern continental crust. Melting of the downgoing slab within the Archean would have prevented the separation of Eu from the rest of the REEs.

Serpentine is the dominant mineral within the subducting oceanic crust and is the source of mobile hydrothermal fluids beneath volcanic arcs. Serpentine samples were collected from the Franciscan Complex in northern California. Samples were powdered and loaded into a 1 atm tube-furnace and held at 600 °C for durations of 1 hour to 10 days. Exsolved aqueous fluids will migrate to grain boundaries and evaporate, potentially leaving a residue of soluble components on the surfaces of dehydrated run products. We used High-Resolution Inductively Coupled Mass Spectrometry (ICPMS) and X-Ray Diffraction (XRD) to characterize both our starting material and our experimental run products. We utilized HCl (rather than HF) dissolution in ICPMS sample preparation in an attempt to recover only the outer REE residue and not the silicate interior of the Eu-rich grains. The ICPMS analysis would yield a REE pattern with a negative Eu anomaly, similar to continent forming arc magmas.



Schematic illustration of hypothesized element mobility in 1 atm dehydration experiments: 1) REEs dissolve in aqueous fluids generated by dehydration of serpentine, while Eu partitions into Al-bearing phase; 2) Aqueous fluid migrates to grain boundary; 3) Aqueous fluid evaporates into air, leaving REE-rich residue on grain surface. Immobile Eu remains within dehydrated mineral grains.

References

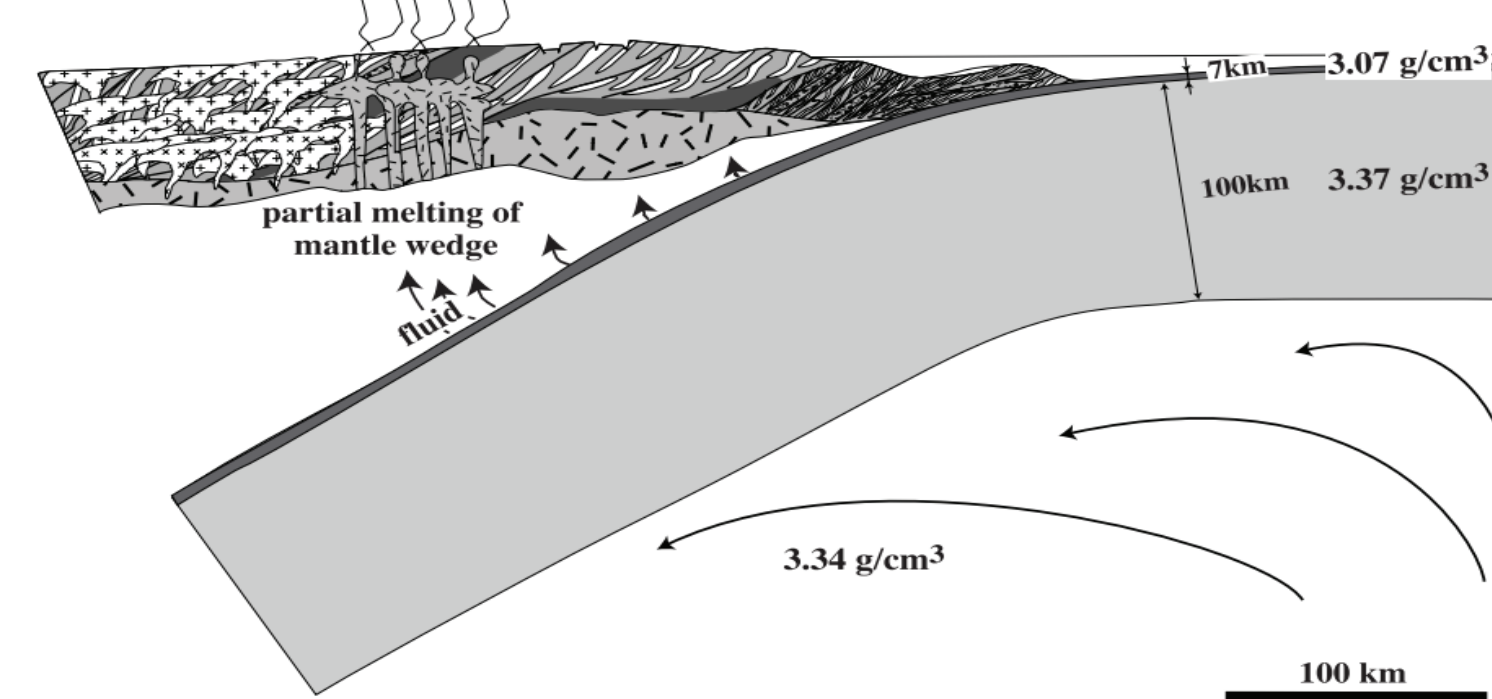
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Motivation for Study

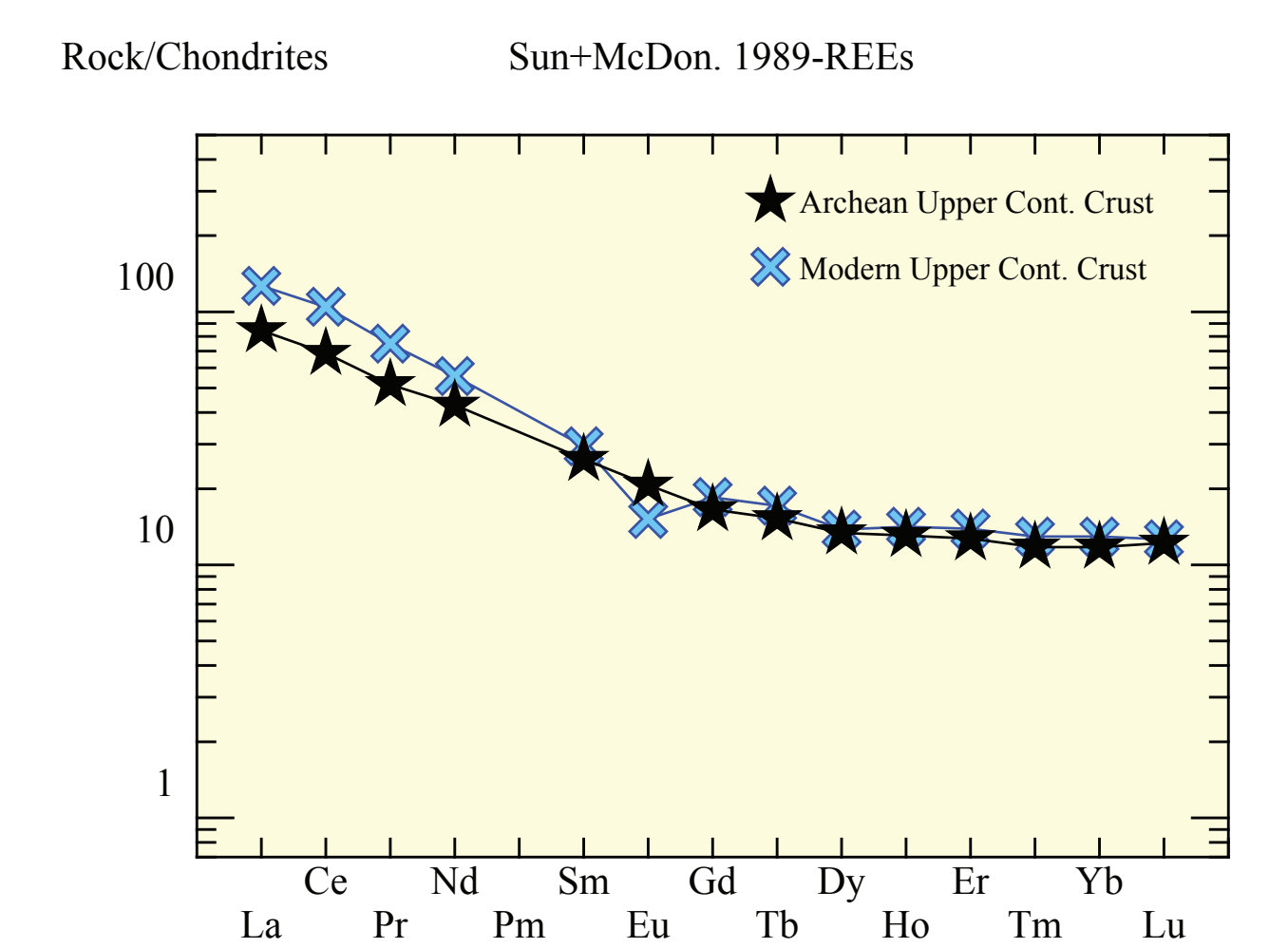
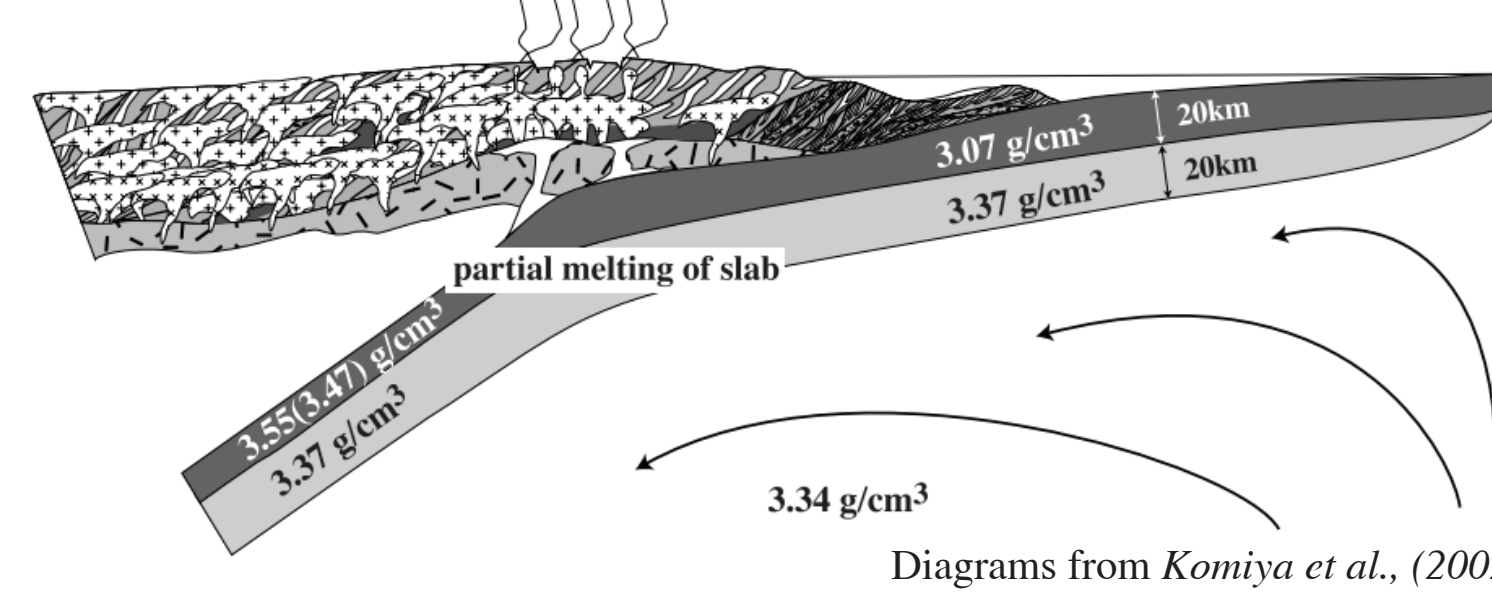
Much debate surrounds the mechanism for generating continental crust. Two distinct geochemical types of juvenile continental crust are recognized in the literature: Type I (the standard 'andesite model'), formed by mantle melting triggered by fluid release from oceanic crust in subduction zones; and Type II (Archean 'TTG assemblages'), formed by the direct melting of subducted oceanic crust. These two types of crust were identified based on their distinct Rare Earth Element (REE) patterns.

Continental crust produced after 2.6 Ga dominantly consists of Type I material and is characterized by a **significant negative Eu anomaly** (Rudnick, 1995) and flat HREE patterns. Many questions regarding the origin of this material remain. For example, intracrustal differentiation (through crystallization of feldspar) has been proposed as a means of producing the Eu anomaly, yet lower crustal xenoliths fail to show a complementary Eu enrichment. Some researchers invoke delamination of an eclogitic lower crust to explain this discrepancy (Rudnick, 1995), but feldspar-rich rocks are not expected to sink through the ultramafic mantle.

Type I: Andesite Model



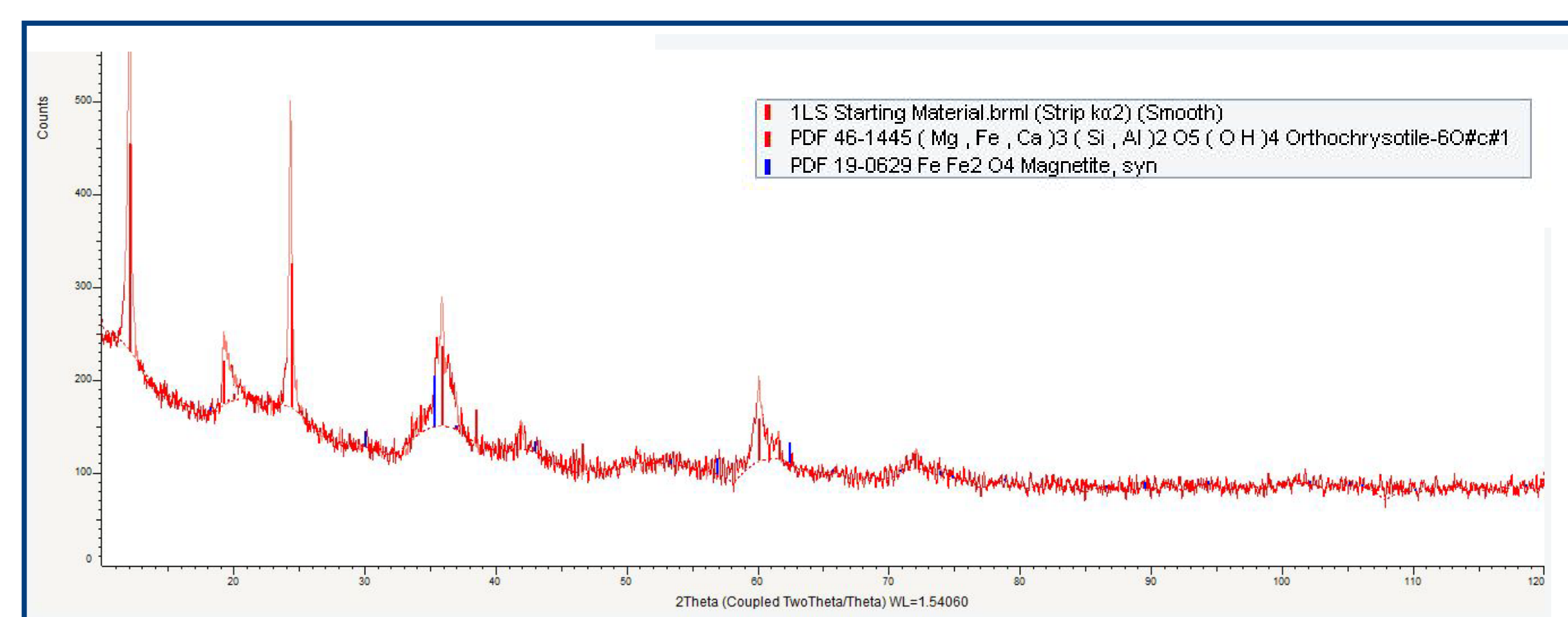
Type II: Archean Model



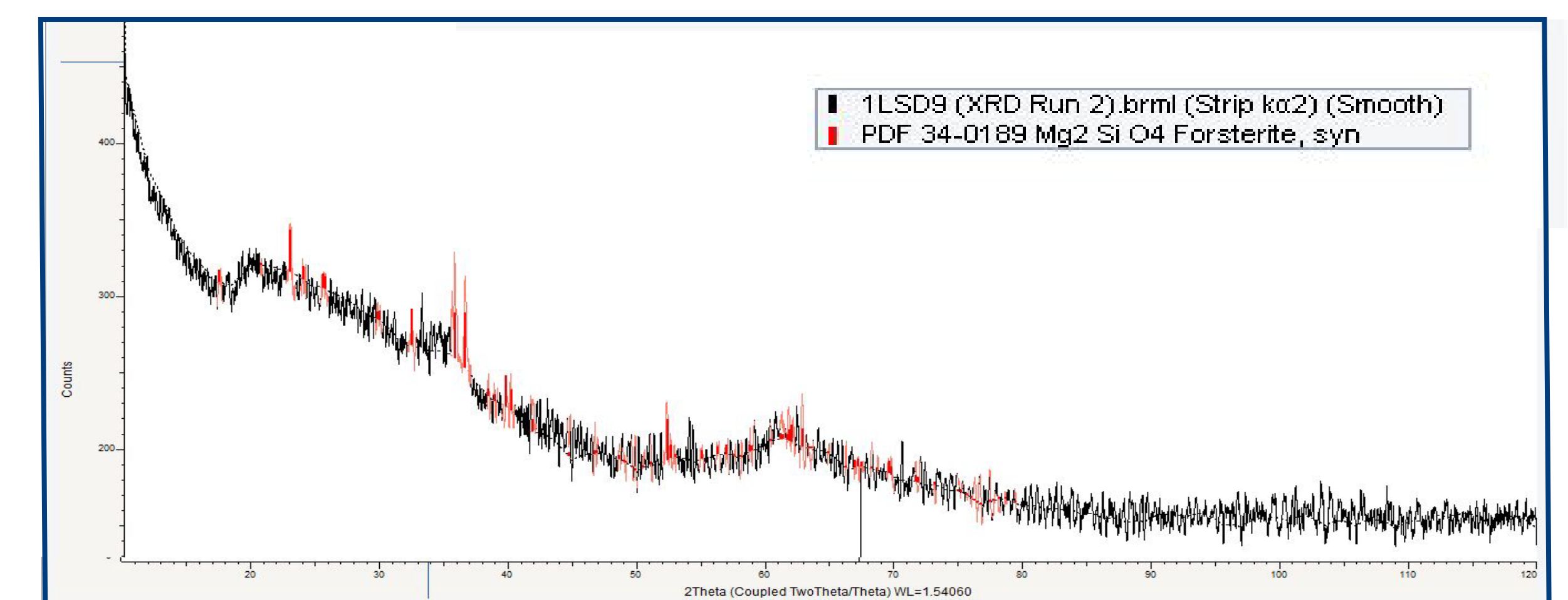
Left: Type I model for modern crustal formation by dewatering of slab and melting of mantle wedge. Type II model for Archean crustal formation by melting of subducting slab.

Right: REE concentrations normalized to chondritic abundance in the Archean and modern upper continental crust.

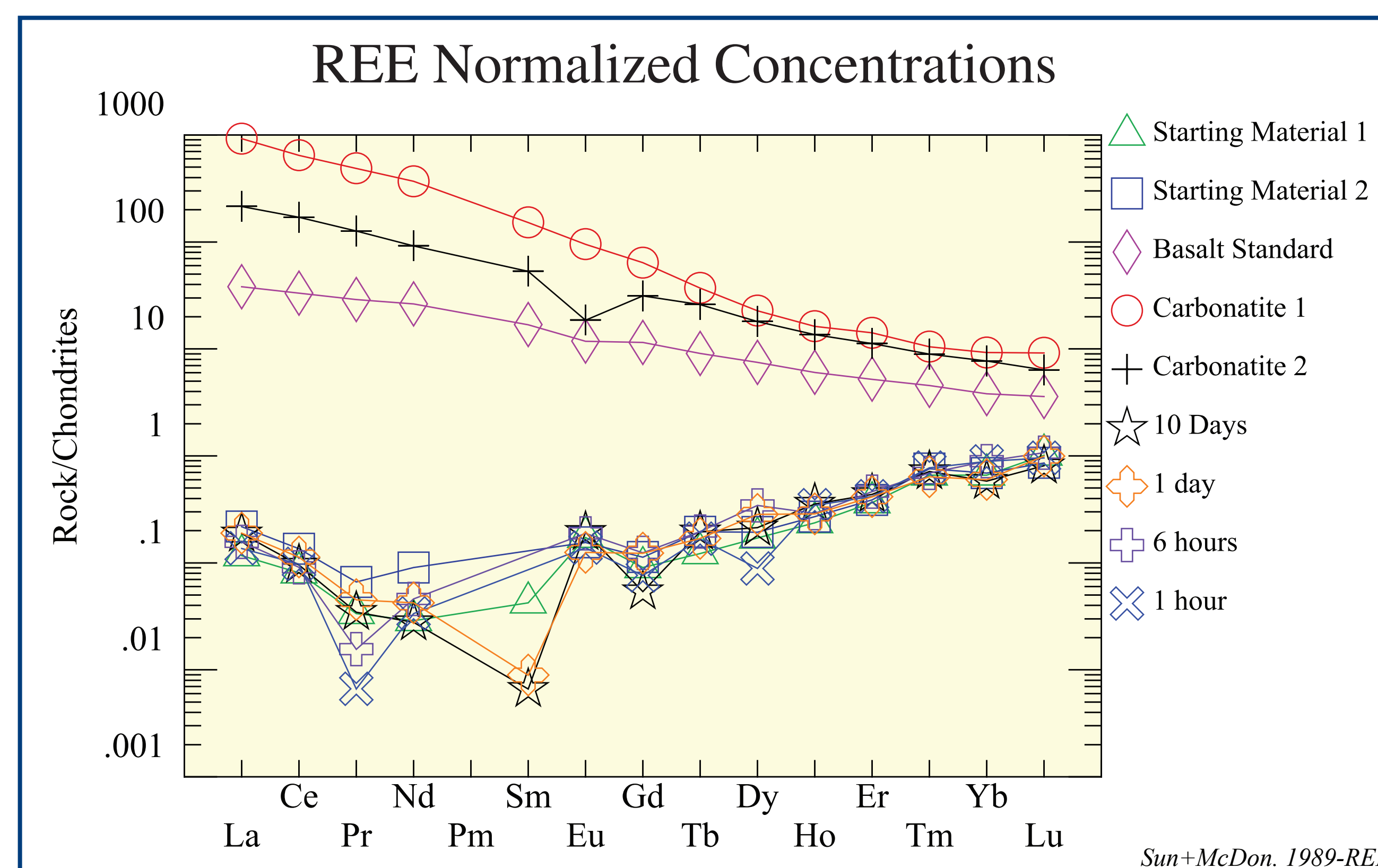
Results



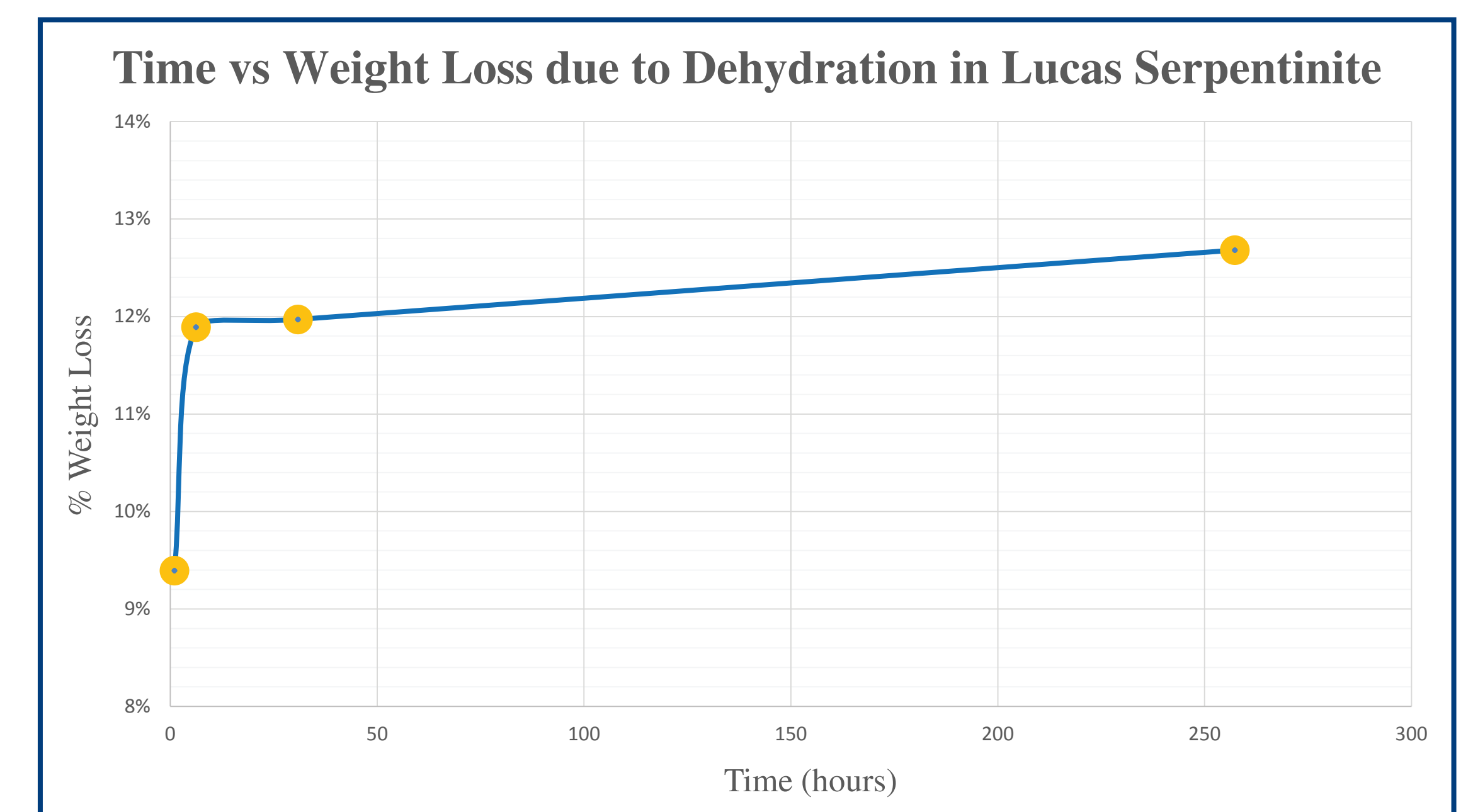
XRD spectra of Lucas Serpentine starting material
• Predominantly composed of orthochrysotile (serpentine group mineral)
• Includes small amounts of magnetite



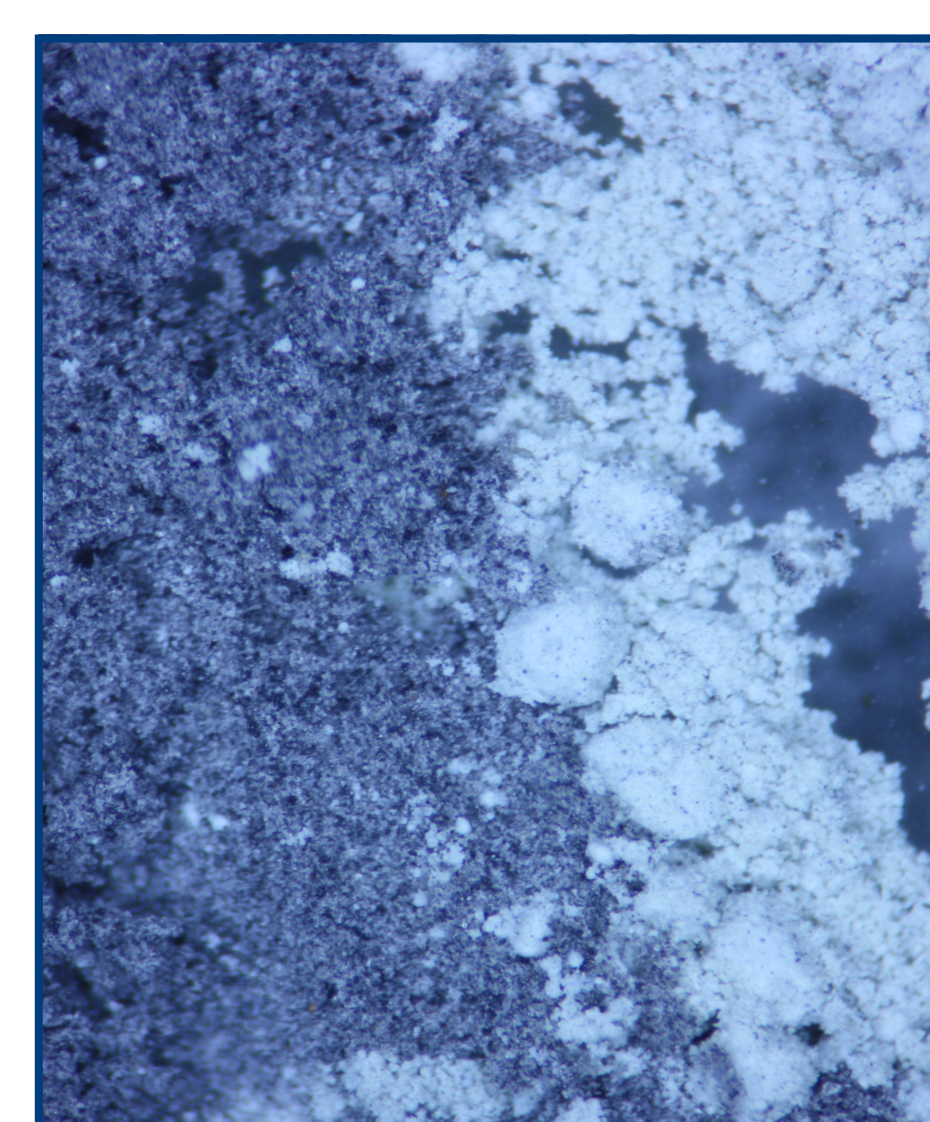
XRD spectra of 10 day sample run
• Run products regressed to forsterite (common mineral in basalt)
• Shorter durations included maghemite, a defect spinel derived from magnetite by replacing Fe²⁺ with Fe³⁺ and vacancies



REE spider diagram normalized to chondritic abundance
• HCl dissolution failed to recover REEs from both serpentine starting materials and forsterite-rich run products
• HCl dissolution successfully recovered REEs from the USGS Standard BHVO powder and two natural carbonatites from Montana



Plot of Time (hours) vs % Weight Loss
• Equilibrium weight loss of ~12-13% at 600 °C and 1 atm
• Maximum weight loss observed after ~6 hours
• Weight loss due primarily to dehydration (water loss)



Differing Powders
Photo comparing powders of BHVO basalt standard (black; left), in which REEs were extracted through HCl dissolution, and Lucas Serpentine starting material (white; right), in which REEs were not extracted through HCl dissolution

Discussion

- Experimental results of REE mobility in dehydrating serpentine failed to meet hypotheses.
 - HCl failed to extract REEs from serpentine starting materials and run products.
- Because the REE concentrations of our dehydration experimental run products were similar to the REE concentrations of our starting material, our initial hypothesis is not discredited, but rather the HCl dissolution failed to extract the REEs from our samples.
- Natural carbonatites fail to show expected positive Eu anomaly.
- The lack of a positive Eu anomaly in two analyzed Montana alkalic rocks requires us to re-think our original model for the origin of the negative Eu anomaly in post-Archean arc magmas.

What's Next?

Further dehydration runs are necessary to constrain the mobility of europium in subduction zone dehydration. High-temperature/high-pressure experiments, with the ability to extract the supercritical fluid during dehydration, are likely required to adequately simulate dehydration within subduction zones.

Acknowledgements

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