The Lu-Hf system and the timing of early planetary differentiation

E.E. SCHERER

Institut fuer Mineralogie, University of Muenster, Germany (escherer@uni-muenster.de)

The ^{176}Lu-^{176}Hf system ($T_{1/2}$ = 37.13 Gyr [1-3]) provides a versatile chronometer and geochemical tracer that is useful for placing constraints on the early silicate differentiation events on planetary bodies. Lu-Hf isochrons from rock suites or minerals within a single rock can directly date magmatic or metamorphic events, setting firm lower limits on the age of crust stabilization. In addition, the initial ^{176}Hf/^{177}Hf values derived from isochrons (or low-Lu/Hf, U-Pb datable minerals such as zircon) can be used to trace the ^{176}Hf/^{177}Hf versus age of distinct reservoirs within the planetary body, thereby dating the first major silicate differentiation events. (e.g., [4, 5] The initial ^{176}Hf/^{177}Hf values of the oldest samples can constrain the Lu/Hf ratios of mantle and crustal reservoirs, thus hinting at the residual mineral phases involved during their production [e.g., 6]. Prerequisites to using the Lu-Hf system as outlined above are a well-defined ^{176}Lu decay constant (λ^{176}Lu) and known bulk ^{176}Hf/^{177}Hf and ^{176}Lu/^{177}Hf values of the planetary body investigated. Values of λ^{176}Lu determined by calibration of Lu-Hf- against U-Pb ages in terrestrial samples [1-3] are consistent and have been corroborated by some results from meteoritic samples [e.g., 7]. Applying this λ^{176}Lu to other meteorites however results in ages that are older than the solar system. Various reasons for this have been proposed, including photoexcitation by gamma radiation [8] or cosmic rays [9], which may have temporarily increased the effective decay rate of ^{176}Lu, creating spurious high apparent λ^{176}Lu values for some meteorites. The ^{176}Hf/^{177}Hf and ^{176}Lu/^{177}Hf of the bulk silicate Earth are assumed to be identical to those of CHUR, which have been difficult to define [10] and are still undergoing refinement [11]. These limitations, as well as the numerous advantages of the Lu-Hf system, will be discussed with regard to early differentiation of the Earth, the Moon, and Mars.

[1] Scherer *et al.* (2001) *Science* **293**, 683-687. [2] Scherer *et al.* (2003) *Meteor. Plan. Sci.* **38 (7) suppl.**, A136. [3] Söderlund *et al.* (2004) *EPSL* **219**, 311-314. [4] Amelin *et al.* (1999) *Nature* **399**, 252-255. [5] Harrison *et al.* (2005) *Science* **310**, 1947-1950. [6] Beard *et al.* (1998) *GCA* **62**, 525-544. [7] Amelin (2005) *Science* **310**, 839-841. [8] Albarède *et al.* (2006) *GCA* **70**, 1261–1270. [9] Thrane *et al. GCA* **71 (15) suppl.**, A1020. [10] Patchett *et al.* (2004) *EPSL.* **222**, 29-41. [11] Bouvier *et al. GCA* **71 (15) suppl.**, A116.

Marcasite in black shales – A mineral based indicator of "burndown" in ancient sapropels?

JUERGEN SCHIEBER

Department of Geological Sciences, Indiana University, Bloomington, Indiana 47405 (jschiebe@indiana.edu)

Although not commonly considered a feasible mineral in early marine diagenesis, marcasite has been observed in marine lag deposits from multiple locations and ages. Textural studies of these lags show that marcasite precipitation was preceded by destruction of reworked pyrite grains, suggesting that, consistent with bottom current reworking, re-oxidation of pyrite produced the low-pH conditions required for marcasite formation.

Application of electron backscatter diffraction (EBSD) was essential for positive identification of marcasite in marine lags, and allows identification of sub-micron crystallites. In a follow-up study EBSD was applied to fine grained iron sulfides within black shales and detected fine-crystalline marcasite. The examined black shales were Ordovician through Cretaceous in age and were collected from outcrops, drill core, and ODP cores (OAE-1a). All, including the Aptian (OAE-1a) sample contained marcasite.

A common feature in these shales is the overgrowth of radial fibrous marcasite on pyrite framboids. When examined closely, these pyrite framboids typically show corrosion and etching prior to marcasite overgrowth. Associated textural features are dissolution of carbonate grains (e.g. shell fragments) prior to marcasite emplacement, as well as coeval deposition of authigenic silica. Judging from differential compaction features, marcasite growth occurred while the sediment was essentially uncompacted.

The observed features are consistent with a scenario where early formed sedimentary pyrite was partially re-oxidized and produced the low-pH conditions that allowed precipitation of marcasite and silica. Given the limits on downward diffusion in fine-grained sediments, this suggests that the associated chemical reactions took place in the uppermost 10 cm's of the sediment. They are most likely the result of a downward moving oxidation front and analogous to burn-down as described from Mediterranean sapropels. Whereas trace-metal based anoxia proxies are largely empirical in nature, marcasite in marine shales represents a definite indication of bottom water oxygenation because oxidation of earlier formed sulfides is required to force low pH conditions. This study also suggest black shales associated with OAE-1a were not deposited under conditions of long term bottom water anoxia.