

The Shergottite Chronology Debate: In Support of Young Igneous Crystallization Ages

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The shergottite meteorites provide powerful constraints on early differentiation in Mars ([1,2] and references therein). These constraints depend on having well determined igneous crystallization ages for the rocks, from which initial ratios for radiogenic isotope systems are calculated. Shergottite ages interpreted to be igneous, ranging from 474 to 166 Ma have been obtained from internal isochrons using the Lu-Hf, Sm-Nd, and Rb-Sr systems (e.g. [1,3]). Recently, these young igneous crystallization ages have been called into question [4,5,6]. Secondary Pb-Pb isochrons for different shergottites give purportedly circa 4.1 Ga ages and have been interpreted to be the true igneous ages while the younger ages represent resetting from shock or fluid-rock interaction [4,5,6].

This issue is examined here by first presenting the petrological, mineralogical, and lithophile isotope evidence that supports the young ages as being igneous. Second, these relationships are evaluated using Re-Os isotopes [7]. One strong piece of supporting evidence for young ages is the EETA 79001 Re-Os isochron (Figure 1). The two lithologies sampled come from portions of the meteorite several centimeters apart, give an isochron age of 164 ± 12

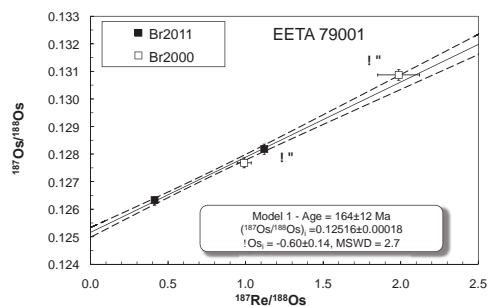


Figure 1: Re-Os isotope systematics of EETA 79001, modified from [7]. A and B designate fractions analyzed from lithologies A and B, respectively. Data from [7] – Br2011, from [8] – Br2000.

Ma ($\pm 2\sigma$), concordant to internal mineral isochron ages for ^{87}Rb - ^{87}Sr of 173 ± 10 , 177 ± 12 , and 174 ± 3 Ma, for ^{147}Sm - ^{143}Nd of 169 ± 23 Ma, for ^{238}U - ^{206}Pb of 150 ± 15 Ma, and for ^{232}Th - ^{208}Pb of 170 ± 36 Ma [9,10,11]. It is not likely possible to generate such systematics from shock unless diffusion rates are orders of magnitude faster than expected. Additional evidence will be presented that examines this issue.

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Replacement of Barite by Radiobarite at close to equilibrium conditions and room temperature

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The solubility control of Ra by coprecipitation of a $\text{Ra}_x\text{Ba}_{1-x}\text{SO}_4$ solid solution has been demonstrated in many cases and can be modeled reliably (Doerner & Hoskins, 1925). However, an open question is whether a Ra containing solution will equilibrate with solid BaSO_4 under repository relevant conditions. Here, Radium enters a system in which barite is in equilibrium with the aqueous solution. Previous studies have indicated that Ra uptake is not limited by pure adsorption but involves a significant fraction of the bulk solid, i.e. barite partially or fully recrystallizes to radiobarite (Bosbach et al., 2010; Curti et al., 2010). Here, we present experimental data from batch recrystallization experiments at room temperature in which a pure barite solid was put into contact with an aqueous solution with an initial Ra/Ba ratio of 0.3 ($5 \cdot 10^{-6}$ mol/L Ra) at neutral pH. Two barites of different morphology and surface area were used during the recrystallization experiments at close to equilibrium conditions and with variation of solid to liquid ratio.

The experimental results show a decrease of the Ra concentration to $3.5 \cdot 10^{-9}$ to $7 \cdot 10^{-9}$ mol/L within the first 70 days of the experiment at a solid/liquid ratio of 5 g/L. At a solid/liquid ratio of 0.5 g/L a slower decrease of the Ra concentration to $2 \cdot 10^{-8}$ mol/L is observed after 180 days. The decrease of the Ra concentration is apparently not related to the specific surface area of the barite crystals. The final radium concentrations are in the range as can be expected from thermodynamic calculations assuming full reequilibration of the barite to a $\text{Ra}_x\text{Ba}_{1-x}\text{SO}_4$ solid. Different thermodynamic models describing the mechanism of Ra incorporation into barite are discussed: (1) Ba – Ra exchange into the crystal volume, combining the Ra – Ba exchange with the Ba – Ba recrystallization rate at equilibrium conditions (Curti et al, 2010); (2) the formation of a Ra-Ba-Phase on barite surfaces. The formation of a Ra-Ba phase on the barite surfaces could be possible because all experiments are already slightly supersaturated with regard to $\text{Ra}_x\text{Ba}_{1-x}\text{SO}_4$ after about one day. Crystallization rates calculated according to this model are in a similar range for all experiments when normalized to the barite surface area.

The results of this study will provide the basis for further spectroscopic and microscopic investigations in order to obtain a molecular-level understanding of the Ra incorporation into barite.

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[3] Curti, E.; Fujiwara, K.; Iijima, K.; Tits, J.; Cuesta, C.; Kitamura, A.; Glaus, M. & Müller, W. (2010) *Geochimica et Cosmochimica Acta*, **74**, 3553–3570