^{182}Hf-^{182}W chronometry for diogenites: Implications for the evolution of the HED parent body

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The Howardite-Eucrite-Diogenite (HED) clan consists of basalts, cumulate gabbros and orthopyroxenites, and probably originated from the asteroid 4 Vesta. Many models have been proposed to explain the petrogenesis of the HED parent body, however, it appears that no single model can accommodate all the observations, and also that HED meteorites might have formed by different igneous processes [1]. In order to better constrain the genetic relationship among the HED meteorites, a suite of diogenites and howardites have been analyzed with the short-lived ^{182}Hf/^{182}W chronometer in order to better understand the petrogenetic history of the HED parent body.

Similar to the eucrites, the bulk diogenites and howardites also show super-chondritic ε_W, varying from +10 to +21, and Hf/W ratios. In addition, the diogenite and howardite data seem to fall on the bulk eucrite isochron [2, 3], even though the data are more scattered. Furthermore, bulk rock and the metal fraction extracted from the diogenite MET00436 seem to form a straight line with a positive slope equivalent to a ^{182}Hf/^{180}Hf initial of $(3.7 \pm 2.2)\times10^{-5}$, and an apparent age of 13.6 myrs post-CAI. Despite the large uncertainty associated to the isochron age of MET00436, it is consistent with the Hf-W isochron ages of numerous eucrites [3], which was interpreted to reflect a late thermal metamorphic event occurred after the formation of HED clan meteorites. As expected, diogenites exhibit much lower Hf and W concentrations and lower Hf/W ratios compared to the eucrites. If diogenites were residues after the extraction of eucrites, they should have higher Hf/W than the eucrites, unless W became less incompatible than Hf due to more oxidized condition. These preliminary data suggest that the HED seems to formed around the same time, Given that they all lie on the bulk eucrite isochron, although more precise isochron ages for additional diogenites and howardites are needed in order to decipher whether if HED clan meteorites were indeed co-genetic.

[1] Barrat J.A. *et al.* (2006) *Meteor. Planet. Sci.* **41**, 1045-1057. [2] Quitté G. *et al.* (2001) *Earth Planet. Sci. Lett.* **184**, 83-94. [3] Klein T. *et al.* (2004) *Geochim. Cosmochim. Acta* **68**, 2935-2946.

Influence of variable phanerozoic seawater chemistry on the form and rate of $CaCO_3$ nucleation

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Background

There is now strong evidence, primarily from fluid inclusions in halite found in marine evaporites, that during the Phanerozoic Eon major variations have occurred in the ratios of the major seawater components. Attention has primarily focused on the variation of the ratio of $Mg^{2+}$to Ca^{2+} and its influence on the precipitation of aragonite versus calcite. This has resulted in considerable literature on the topic of "aragonite seas", represented by current and Permian seawater with a high Mg^{2+} to Ca^{2+} ratio (~5), versus "calcite seas", represented by a low (~1) Mg^{2+} to Ca^{2+} ratio. Previous research in our lab (1) demonstrated that the critical Mg^{2+} to Ca^{2+} ratio for calcite precipitation was 1.4 ± 1 at 25 °C and strongly depended on temperature. Only the Mg^{2+} concentration was varied in the previous study.

Results

Experiments were conducted by the methods used in (1) where slow degassing of CO_2 results in a gradual increase in supersaturation until nucleation occurs. Modern seawater and seawater of estimated Albian Cretaceous composition (Mg^{2+} to Ca^{2+} = 1.3 and lower SO_4^{2-}) were studied. Factors, such as supersaturation at nucleation, time to nucleation, rate of approach to nucleation and pCO_2 at nucleation, not previously measured were examined.

The supersaturation at which nucleation occurred depended on the rate at which nucleation was approached and pCO_2. The air-water and bubble-water interfaces were observed to be favored sites of initial nucleation. Minimal supersaturations with respect to aragonite at nucleation with $pCO_2 \approx 2000$ µatm were ~30 in modern seawater and ~10 in Albian seawater. In the Albian-composition seawater, calcite nucleated first when the pCO_2 at nucleation was <2500 µatm and then was overgrown by calcite as the Mg^{2+} to Ca^{2+} rose during precipitation. At higher pCO_2 values at nucleation in Albian seawater, and in modern seawater, only aragonite formation was observed.

[1] Morse *et al.* (1997) *Geology* **25**, 85-87.