# Origin of spherulitic concretions in Cambro-Ordovician black shales, St. Lawrence Estuary, Quebec, Canada

REINHARD HESSE<sup>1\*</sup>, CHRISTOPHER FONG<sup>2</sup>

<sup>1</sup>Earth & Planetary Sciences (McGill), Montreal, Canada, <u>Reinhard.Hesse@mcgill.ca</u>

<sup>2</sup> Apt. 102, No.16, Lane 3292, Hongmei Road, Shanghai, 201103 China, Fongchristopher@hotmail.com

#### **Introduction and Results**

Spherulitic concretions are very rare among carbonate concretions which are a trademark of organic-matter rich sediments and normally consist of micritic carbonate. The occurrence in Cambro-Ordovician black shales of unknown stratigraphic age on mid-channel islands in the St. Lawrence Estuary in Quebec is among four hitherto known examples [1,2,3] of spherulitic concretions and their origin is still poorly understood. These concretions occur in close association with and show various transitions to cone-in-cone structure. The spherules are 0.5 to 12 mm in diameter. They consist of intergrown fine fibers of ferroan calcite and quartzine, pointing to the formation of the concretions below the sulfate reduction zone. A phenomenological theory of spherulitic crystallization [4] relates the thickness  $\delta$  of an impurity-rich layer in front of impurity-rejecting growing crystals to the impurity-diffusion coefficient D and the growth velocity G of the crystal by  $\delta$ =D/G. In spheruliteforming environments, extremely small values of  $\delta$  (on the order of <10<sup>-4</sup>cm) in conjunction with cellulation lead to spherulitic fibre growth. The intimate association of calcite and quartzine in the concretions seems hard to understand. Most spherules precipitated experimentally in the laboratory crystallized in a gelatinous medium in the presence of impurities. Silica gel is the most common medium used. The occurrence of silica gel has not been reported from clastic or biogenic siliceous pelagic deep-sea sediments, not even in hydrothermally sourced ponds of mid-oceanic ridges. However, experimental spherulite precipitation has also been achieved from alkaline aqueous solutions. Alkaline conditions are established during early diagenesis in the lower sulfate reduction zone so that fibrous calcium carbonate precipitation in the presence of impurities may easily start in the carbonate-reduction (methane-generation) zone. The switch from carbonate precipitation to silica precipitation into the pore spaces of coarse, open-texture fibrous carbonate spherulite may be achieved by the dissolution of sponge spicules or radiolarians which would lead to low supersaturation allowing the direct precipitation of quartzine.

#### Conclusion

Intergrown spherulitic carbonate/quartzine concretions seem to require special chemical conditions of pore-water composition and burial-diagenetic evolution that may shed important light on unusual early diagenetic chemical environments. Sperulitic concretion growth can be explained in view of a phenomenological crystallization theory [4] and experimental results.

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## New insights into the origin of the Shatsky Rise from Sr-Nd-Pb-Hf isotopes of volcanic rocks from IODP Exp. 324

KEN HEYDOLPH<sup>1\*</sup>, JOERG GELDMACHER<sup>1</sup>, KAJ HOERNLE<sup>1</sup>

<sup>1</sup>GEOMAR | Helmholtz Centre for Ocean Research, Kiel, Germany, kheydolph@geomar.de (\* presenting author) jgeldmacher@geomar.de khoernle@geomar.de

### Shatsky Rise: a unique large igneous province

The submarine Shatsky Rise plateau, situated in the northwest Pacific Ocean ca. 1500 km east of Japan, is the only large intraoceanic plateau, which formed during the Late Jurassic to Early Cretaceous at a time period with numerous reversals of the Earth's magnetic field. Combined with bathymetric data, the magnetic reversals allow a detailed reconstruction of the original tectonic setting, spatial evolution and approximate seafloor age from the magnetic record [1]. Accordingly, the three main volcanic edifices Tamu, Ori, and Shirshov massifs formed by massive volcanism during a short time span along a southwest - northeast trending, rapidly spreading triple junction. After the initially voluminous stage, which created the large Tamu massif, the volcanism waned to less voluminous phases, creating Ori and eventually the smallest Shirshov massif.

We present here Sr-Nd-Pb and Hf isotope data from relatively fresh basaltic lava flows from Site U1347A drilled during IODP Expedition 324 and Site 1213B (ODP Leg 198) both located on the southernmost (oldest) volcanic edifice of Shatsky Rise. Initial <sup>143</sup>Nd/<sup>144</sup>Nd: 0.512903 to 0.512981 and <sup>176</sup>Hf/<sup>177</sup>Hf: 0.283076 to 0.283100 isotopic compositions from Site U1347A samples are quite uniform throughout the entire hole and show neither distinct MORB nor intraplate (Ocean Island Basalt) affinity. Site 1213 samples are slightly less radiogenic in Nd and Hf isotopic compositions. In a Nd vs. Hf isotope plot Site U1347 form a tight cluster at the edge of the Pacific MORB field below the present-day Hf-Nd mantle array. Site 1213 samples have less radiogenic Nd and Hf isotopic compositions. Although initial Pb double spike <sup>206</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb isotopic compositions for Site U1347 range from 18.13 to 18.46 and 37.71 to 37.96 respectively and overlap with MORB-like compositions, they trend towards more radiogenic, intraplate-like values.

In general, our isotopic data from Tamu massif show a very homogeneous and relatively depleted isotopic composition. Such composition could reflect a large degree of melting, consistent with an origin of the initial (oldest) phase of Shatsky volcanism from an arriving hot plume head [2].

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