

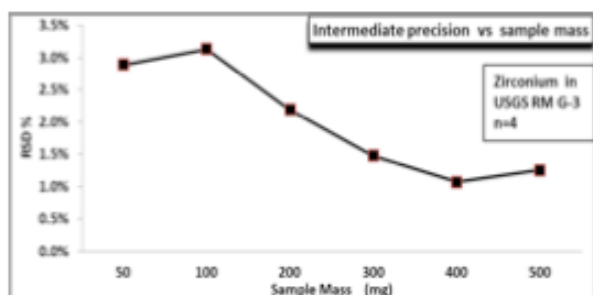
The determination of homogeneity of geological reference material

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Reference materials (RM) support measurements in geological research due to the degree of homogeneity, traceability and confidence interval of their property values. Homogeneity testing is essential in certification of reference materials, as it should demonstrate the validity of the certified values and their uncertainties. Ingamells sampling theory [1] has been applied to test homogeneity of IAG Candidate RM trachyandesite (MTA), rhyolite (MRH), RM CGL MGL-AND andesite and uncertified USGS Granite (G-3). The sample digestion for test portions 50 mg to 500 mg was performed following the protocol [2] by sodium peroxide sintering and measurements with ICP-MS.

It is proposed that at least 300 mg is the minimum test portion size for trachyandesite (MTA) and Granite G-3 and 100 mg test portion for Rhyolite (MRH) and MGL-AND andesite to assure acceptable precision less than 2%. Complete digestion of all the analytes including mineral zircon is possible with sample/Na₂O₂ ratio 1:6.



In establishing reference values for reference materials, the contribution of detectable heterogeneity to the overall uncertainty of individual reference values has been quantified. The method has been developed to recover all analytes in particular zircon for 50 mg test portion size but it is suggested that 50 mg test portion is not representative for the particular rock types. It is also recommended to use ICP-MS as a tool of analysis as WD-XRF cannot determine homogeneity in specified test portion due to lower detection limits.

[1] Ingamells & Switzer (1973) *Talanta* **20**, 547-568.

[2] Meisel *et al. Geostand. Newsl.* **26**, 53-61.

Isotopic Studies of Rapid Carbonate Precipitates

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In geologic systems, where crystallization is *rapid*, the carbonate isotopic systems may be out of equilibrium. Our studies of well scales in hydrocarbon production tubing and tunnel speleothems indicate carbonate to be out of equilibrium when growth rates exceed mm/year. Calcite scales resulting from CO₂ degassing results in covariance in ¹³C and ¹⁸O of the precipitate where the limited CO₂ degasses from a thin fluid film. Vaterite occurrences have extremely light isotopic values (>10 per mil) relative to calcite scales in the same reservoir.

Recent experiments to sequester CO₂ from coal combustion involve *extremely rapid* CaCO₃ precipitation, and oxygen values 10 to 20 per mil lighter than expected for equilibrium. These observations suggest that during extremely rapid crystallization rates the low mass light isotopes are preferentially incorporated into the carbonate, as observed by McCrae [1]. Light isotopes may reach the reaction site, and may form CaCO₃ species in solution more rapidly, once crystallization rates exceed some threshold rate. We are currently conducting experiments to determine the relation between crystallization rate, carbonate poly morph type, and stable isotopic composition, by CaCO₃ precipitation by CO_{2(g)} addition at different CO₂ partial pressures in calcium chloride solutions at neutral pH.

[1] McCrae, J.M. (1950) *J. Chem. Phys.* **18**, 849-857.