

CHEMICAL AND ISOTOPIC STUDY OF DEEP SEA SPHERULES

D. A. Papanastassiou, D. E. Brownlee¹, and G. J. Wasserburg, Lunatic Asylum, Div. Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; ¹and Dept. Astronomy, U. Washington, Seattle, WA 98195.

We report on mineralogical, chemical, and Rb-Sr isotopic studies of individual deep sea spherules. These spherules are thought to be produced from meteoroids by ablation during their passage through the earth's atmosphere and have undergone alteration in the marine environment. These materials may provide samples of diverse meteorites as well as of meteors which have orbital parameters indicative of cometary origin. We sought to improve and apply microanalytical techniques for Rb-Sr measurements for samples containing 10^{11} - 10^{12} atoms of Sr [1]. The purpose was to establish the extent to which the Rb-Sr systems are consistent with derivation of the stony deep-sea spherules (DSS's) from extraterrestrial materials of chondritic composition, as proposed based on their mineralogy and major element composition (cf. review by Brownlee [2]). The DSS's have been collected by pulling a magnetic sled ("cosmic muck rake") across the sea floor, at a depth of 5,000 m, 1,000 km east of Hawaii [3]. A large fraction of the collected material ($\leq 50\%$) was found to be of possible extraterrestrial origin and to be composed of olivine, glass, and magnetite [2,4]. The DSS's were handpicked and cleaned ultrasonically in water and isopropanol. The spheres were potted and ground for electron microprobe analyses. Broad beam analyses are shown in Table 1. The data show a relatively uniform chemical composition similar to chondritic abundances for the major refractory elements. The DSS's were then extracted using dichloroethane, washed in isopropanol and water, and dissolved in HF and HNO₃ in micro-environmental chambers. Contamination for the sample dissolution and handling procedures was found to be $(7-10) \times 10^8$ atoms for Rb and $(2-6) \times 10^9$ atoms for ⁸⁸Sr. DSS solutions were split into two aliquots, one of which was spiked using a mixed Rb-Sr tracer. Both aliquots were analyzed following the modified direct loading procedures [1]. The data (Table 2) show good agreement for the ⁸⁷Sr/⁸⁶Sr compositions from spiked (sp) and unspiked (co) aliquots. The Rb-Sr data on DSS's show: a) large depletion of Rb relative to Sr; b) the presence of Sr at concentrations of 2-10 ppm; c) the presence of very radiogenic ⁸⁷Sr/⁸⁶Sr from 0.730 to 0.757; d) normal ⁸⁴Sr/⁸⁸Sr. The results show that Sr in the DSS's has a composition distinct from Sr in seawater or in mid-ocean ridge basalts. The Sr in DSS's also appears not to have significantly exchanged with seawater Sr. The observed ⁸⁷Sr/⁸⁶Sr in DSS's are consistent with the range of values obtained for chondritic meteorites. The radiogenic nature of ⁸⁷Sr/⁸⁶Sr shows that Rb must have been depleted from the DSS's recently, presumably by volatilization or by leaching in seawater. It is clear that no meaningful Rb-Sr model ages can be calculated for these DSS's. The Sr concentrations in DSS's are in the range observed for chondritic meteorites. These observations indicate that Sr in DSS's is consistent with provenance from chondritic meteorites and provide support for the formation of DSS's by ablation of meteoroids in the earth's atmosphere. It is not possible to establish whether cometary particles were sampled. The limited data on deep-sea sediments from the Pacific Ocean [5,6] show relatively non-radiogenic ⁸⁷Sr/⁸⁶Sr less than 0.710 and can be excluded as sources for DSS's. Higher ⁸⁷Sr/⁸⁶Sr values of up to 0.740 have been determined for sediments in the Atlantic Ocean which correlate with more ancient continental crustal sources [7,5]. From textural and chemical data it appears highly unlikely that the DSS's are terrestrial detrital materials. The highly radiogenic Sr in DSS's shows that they cannot reasonably be associated with terrestrial materials of such ultrabasic compositions (Mg, Fe-rich, see Table 1). Based on the available data a strong case can be presented that the Sr isotopic composition in

Deep Sea Spherules

Papanastassiou, D. A., et al.

DSS's reflects a preserved extraterrestrial signature, characteristic of chondritic meteorites. We expect in the near future to be able to apply these techniques to (smaller!) interplanetary dust particles. The measurement of the Nd isotopic composition in some of the larger DSS's appears feasible. Div. Contribution No. 3738 (407). Supported by NASA, grant NGL 05-002-188.

Table 1. Chemical Composition of Deep Sea Spherules

	KK1F15	KK1V8	KK1G13	KK1A10	KK1B18	KK1A7	KK1A17
MgO	25.0	30.3	32.0	22.3	22.0	32.6	23.6
Al ₂ O ₃	2.8	2.5	3.2	3.1	2.8	1.1	2.9
SiO ₂	37.8	38.5	46.3	37.8	34.7	41.1	34.5
CaO	1.7	1.8	1.6	3.2	2.0	2.0	2.5
TiO ₂	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cr ₂ O ₃	0.8	0.3	0.2	0.3	0.6	0.04	0.3
MnO	0.3	0.3	0.3	0.3	0.3	0.3	0.1
FeO	33.2	25.8	15.8	30.8	36.5	21.8	32.8
NiO	0.5	0.7	0.04	0.9	1.0	bd	2.7

EMP data, 30µm beam; Na,K were below detection (bd)

Ref: [1] D.A. Papanastassiou and G.J. Wasserburg (1981a,b) in Lunar Planet. Sci. XII,802-804, and Proc. 12th LPS Conf. (in press); [2] D. E. Brownlee (1981) in The Sea, chap.7, ed. C. Emiliani, J. Wiley, 733-762; [3] D.E. Brownlee, L.B. Pilachowski, and P.W. Hodge (1979) in Lunar Planet. Sci. X, 157-158; [4] D.E. Brownlee, B. A.

Bates, L.B. Pilachowski, E. Olszewski, and W.A. Siegmund (1980) in Lunar Planet. Sci. XI, 109-111; [5] M.T. McCulloch and G.J. Wasserburg (1978) Science 200, 1003-1011; [6] S.L. Goldstein and R.K. O'Nions (1981) Nature 292, 324-327; [7] E.J. Dasch (1969) Geochim. Cosmochim. Acta 33, 1521-1552.

Table 2. Rb-Sr Results on Deep Sea Spherules

Sample ^a	F ^b	Rb ^c ⁸⁸ Sr ^c		⁸⁵ Rb ^d ⁸⁷ Rb	⁸⁵ Rb/ ⁸⁸ Sr ^e x10 ⁴	⁸⁷ Sr ^f ⁸⁶ Sr	⁸⁴ Sr/ ⁸⁸ Sr ^f x10 ³	⁸⁷ Rb/ ⁸⁶ Sr x10 ³	
		10 ⁸ atoms	10 ¹² atoms						
KK1F15	sp	0.5	2.4	0.80	0.175	1.0-0.2	0.7404±9g	17	0.7
360x150	co	0.5	2.4	0.80	1.69 ^h	0.5-0.3	0.7393±33	7.09±6 ^h	
KK1V8	sp	0.17	2.8	1.80	0.31	0.7-0.2	0.7421±11	16	0.4
600x300	co	0.17	2.8	1.80	2.59	0.6-0.2	0.7457±8	6.67±2	
KK1G13	sp	0.5	154	0.19	1.53	5.0-1.2	0.7424±35	57	191
350x200									
KK1A10	sp	0.5	6.3	2.0	0.057	1.1-0.2	0.7326±9	31	0.7
400x300									
KK1B18	sp	0.25	3.1	0.40	0.087	0.4-0.05	0.7486±8	42	1.8
360x200	co	0.38	4.7	0.60	2.60	0.3-0.01	0.7478±10	6.67±2	
KK1A7	sp	0.26	28	0.30	0.42	1.9-0.3	0.7565±14	63	22
500x350	co	0.22	24	0.25	2.63	2.0-0.3	0.7548±14	6.70±6	
KK1A17	sp	0.16	25	0.39	0.151	0.7-0.1	0.7303±11	109	15
400x300	co	0.13	20	0.31	2.61	0.6-0.1	0.7320±8	6.69±3	

^aDiameter of original sphere (µm) x height (µm) of the remaining spherical section after grinding. ^bFraction of the dissolved sample used for each M.S. analysis. ^cRb and Sr in the fraction of the dissolved sample used for M.S. analysis. ^dMeasured ratio; differences from ~2.60 reflect the ⁸⁷Rb tracer addition. ^eRatio of ion beam intensities during Sr analysis. ^fUncertainties are 2σ_{mean}; ⁸⁴Sr/⁸⁸Sr uncertainties are given for unspiked samples. ^gFaraday cup data yield 0.7394±8. ^hNon-normal ratios reflect contamination by 3x10⁷ ⁸⁷Rb, 3x10⁸ ⁸⁴Sr atoms from 2x10⁻⁵ g of mixed spike for this aliquot.