

qualifications noted above, the temperature scales defined by the disparate phenomena of kinetic energy release and electron scattering are related; with comparably-sized clusters this relation would presumably be even more evident.

Other techniques, such as laser ablation and sputtering, have also been used to prepare isolated aggregates of matter. The metastability of sputtered copper clusters¹⁵ has already been shown⁶ to be consistent with the evaporative ensemble. We may thus suppose that the scaling described here will be widely applicable. It is required only that each cluster will have undergone at least one evaporation.

This condition is not always met. Valente and Bartell^{3,4} have noted that lower temperatures may be obtained from supersonic expansions when the condensing gas is diluted in a non-condensing carrier. The kinetics of evaporation thus establish only an upper limit to the range of accessible temperatures. Considerable flexibility in the tailoring of the magnetic and other properties of the aggregates remains. We observe, for example, that the Curie points of the common ferromagnetic materials lie below the demarcations given by equation (1).

I thank G. Torchet and A. J. Stace for stimulating communications. This research was sponsored by the Office of Health and Environmental Research, US Department of Energy under contract with Martin Marietta Energy Systems, Inc.

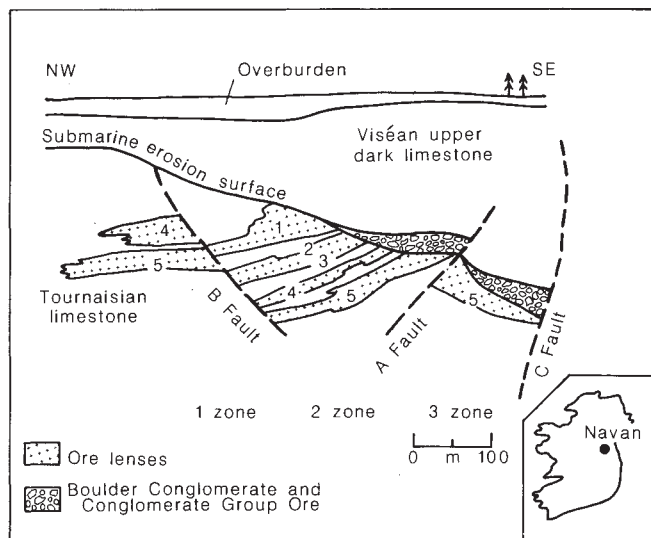


Fig. 1 Generalized cross-section of the Navan orebody showing the lens structure referred to in the text (after Andrew and Ashton²⁹). Inset: map of Ireland showing location of Navan.

Received 23 December 1986; accepted 25 March 1987.

1. Farges, J., de Feraudy, M. F., Raoult, B. & Torchet, G. *Surf. Sci.* **106**, 95-100 (1981).
2. Torchet, G., Schwartz, P., Farges, J., de Feraudy, M. F. & Raoult, B. *J. chem. Phys.* **79**, 6196-6202 (1983).
3. Valente, E. J. & Bartell, L. S. *J. chem. Phys.* **79**, 2683-2686 (1983).
4. Valente, E. J. & Bartell, L. S. *J. chem. Phys.* **80**, 1451-1457 (1984).
5. Klots, C. E. *J. chem. Phys.* **83**, 5854-5860 (1985).
6. Klots, C. E. *Z. Physik D38*, 5 (1987).
7. Trouton, F. *Phil. Mag.* **18**, 54-56 (1884).
8. Huttman, R. et al. (eds) *Selected Values of the Thermodynamic Properties of the Elements* (Am. Soc. Metals, Metals Park, Ohio, 1973).
9. Raznjevic, K. *Handbook of Thermodynamic Tables and Charts* (Hemisphere Publishers, Washington, 1976).
10. Gspann, J. *Physics of Electronic and Atomic Collisions* (ed. Datz, S.) 79-96 (North Holland, Amsterdam, 1982).
11. Klots, C. E. *J. chem. Phys.* **58**, 5364-5367 (1973).
12. Stace, A. J. & Stukla, A. K. *Chem. Phys. Lett.* **85**, 157-160 (1982).
13. Stace, A. J. *J. chem. Phys.* **85**, 5774-5778 (1986).
14. Illies, A. J., Jarrold, M. F., Bass, L. M. & Bowers, M. T. *J. Am. chem. Soc.* **105**, 5775-5781 (1983).
15. Begeman, W., Meiwes-Broer, K. H. & Lutz, H. O. *Phys. Rev. Lett.* **56**, 2248-2252 (1986).

Origin of a giant orebody at Navan, Ireland

H. Mills*†, A. N. Halliday†§, J. H. Ashton‡, I. K. Anderson* & M. J. Russell*

* Department of Applied Geology, University of Strathclyde, Glasgow G1 1XJ, UK

† Scottish Universities Research & Reactor Centre, East Kilbride, Glasgow G75 0QU, UK

‡ Tara Mines, Navan, Ireland

The Navan base-metal deposit in Ireland formed 360 Myr ago¹ and is one of the world's largest orebodies, with 70 million tonnes of 12% Zn+Pb. Much of the mineralization was sedimentary, exhalative: other well known examples of this class of the so-called SEDEX deposits are Mount Isa in Australia, Sullivan in Canada, and Meggen in Germany. Several models for the formation of such deposits have been suggested. Here we report the first systematic stratigraphic Pb isotopic study of galenas in any giant exhalative Zn+Pb orebody. We document evidence that the sources of Pb in the Navan orebody evolved to produce increased dispersion and less radiogenic averages of lead isotopic compositions. This

§ Present address: Department of Geological Sciences, University of Michigan, Ann Arbor Michigan 48109-1063, USA.

is as expected if the orebody formed from a hydrothermal convection cell which expanded to scavenge metals from progressively deeper parts of the continental crust.

Various genetic models have been suggested for the origin of SEDEX base-metal deposits: (1) basin brine expulsion, where saline connate waters dissolve metals from compacting sediments and are expelled upwards during basin subsidence²⁻⁶; (2) a hydrothermal convection system where fluid circulation is initiated and added to by intrusive igneous activity⁷⁻¹⁰; (3) release of metal-bearing waters during metamorphism¹¹⁻¹³; (4) seismic pumping in which fluids fill cracks which have opened up before a shear failure event which then expels the (heated) fluids back upwards¹⁴; (5) downward excavating convection of modified heated saline metalliferous sea water in which, during a period of crustal extension, the fluids penetrate as far as the brittle/ductile transition zone which is advanced to progressively greater depths by the concomitant cooling^{15,16}.

Distinguishing between these models using Pb isotopic compositions is partly based upon observations for other deposits and partly upon expectations derived from the process involved. Basin brine expulsion (model 1) has been most frequently invoked to explain Mississippi Valley type (MVT) deposits. These are commonly found to contain very radiogenic and exceedingly variable Pb isotopic compositions^{17,18}. Deposits of magmatic affiliation (model 2) should have relatively homogeneous Pb isotopic compositions which are similar to those of contemporaneous magmas. Deposits formed by extraction of metamorphic fluids (model 3) obviously would have no specific Pb isotope signature because this would depend simply on what is being metamorphosed¹⁹. We doubt that model 3 is relevant to giant-sized SEDEX deposits, because volumes of metamorphic fluid would probably be relatively small and the major tectonic thickening and metamorphism in this particular region had ceased 40 Myr previously (400 Myr ago). Nonetheless the possibility that a metamorphic basement was involved can obviously be investigated using Pb isotopes provided it has had a different history than that of the overlying crust. Seismic pumping (model 4) has never been invoked as a dominant mechanism in the formation of SEDEX deposits because it is difficult to see how the process can be sufficiently long-lived and powerful to produce major orebodies. It has no specific predictions in terms of lead isotope results. The model of deepening convective systems (model 5) may be tested with a lead isotope experiment. In general terms, high-grade metamorphic

Table 1 Lead isotope analyses of galenas from Navan

Location	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	Location	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
Lens 1				269.5 m			
SH652	18.015 ± 3	15.522 ± 4	37.767 ± 7	SH652	18.070 ± 18	15.564 ± 26	38.023 ± 30
220.5 m				275 m	18.100 ± 6	15.593 ± 15	38.117 ± 20
SH652	18.090 ± 10	15.540 ± 8	37.886 ± 20	Lens 4			
220.5 m	18.105 ± 8	15.549 ± 7	37.920 ± 13	SH652	18.090 ± 6	15.500 ± 9	37.584 ± 17
SH652	17.551 ± 5	15.419 ± 4	37.198 ± 10	297.5 m			
227.5 m	17.560 ± 10	15.425 ± 8	37.203 ± 12	UG226 N	18.185 ± 11	15.575 ± 15	38.075 ± 27
SH652	17.858 ± 10	15.532 ± 5	37.556 ± 13	1,390 Level			
227.5 m				UG226 N	18.115 ± 3	15.580 ± 2	37.970 ± 7
SH652	17.841 ± 12	15.525 ± 11	37.664 ± 21	1,390 Level			
232.5 m				UG253 access	18.215 ± 8	15.553 ± 10	38.022 ± 17
SH652	17.998 ± 10	15.507 ± 15	37.664 ± 30	1,315 Level			
241 m	18.005 ± 12	15.512 ± 17	37.680 ± 35	UG253 access	18.212 ± 10	15.585 ± 8	38.125 ± 16
SH652	17.791 ± 3	15.474 ± 3	37.431 ± 6	1,315 Level			
242.5 m				Lens 5			
SH652	18.202 ± 6	15.644 ± 10	38.386 ± 13	SH652	18.155 ± 4	15.601 ± 4	38.079 ± 7
246.5 m				325 m	18.175 ± 10	15.620 ± 10	38.093 ± 15
UG229 N	18.203 ± 3	15.561 ± 3	38.043 ± 10	SH652	18.222 ± 6	15.610 ± 5	38.191 ± 14
1,435 Level	18.191 ± 7	15.585 ± 10	38.152 ± 14	330.5 m			
UG229 N	18.201 ± 3	15.553 ± 2	38.011 ± 11	SH652	18.186 ± 15	15.542 ± 13	37.968 ± 22
1,435 Level				332.5 m			
UG229 N	18.204 ± 14	15.592 ± 13	38.162 ± 29	SH543	18.170 ± 21	15.554 ± 15	38.056 ± 31
1,435 Level				335 m			
SH543	17.910 ± 2	15.562 ± 3	37.764 ± 8	SH543	18.170 ± 16	15.563 ± 10	38.000 ± 21
224.5 m				338.5 m			
SH543	18.190 ± 19	15.553 ± 13	37.848 ± 27	SH543	18.207 ± 10	15.606 ± 7	38.220 ± 16
252.7 m				330 m			
Lens 2				UGBL6. P8	18.183 ± 15	15.550 ± 13	38.052 ± 21
(1,285 Level)				1,315 Level			
UG2217	18.197 ± 8	15.584 ± 5	38.129 ± 14	Silvermines			
UG6201	18.172 ± 5	15.553 ± 6	38.015 ± 11	SH26	18.161 ± 9	15.528 ± 3	37.933 ± 20
UG6202	18.174 ± 11	15.563 ± 9	37.998 ± 28	4520	18.196 ± 10	15.556 ± 10	38.053 ± 21
UG6203	18.022 ± 15	15.563 ± 9	37.796 ± 22	4700-3	18.173 ± 6	15.544 ± 6	37.982 ± 15
UG6204	18.101 ± 19	15.557 ± 21	37.799 ± 31	Tynagh			
Lens 3				CF123	18.028 ± 4	15.559 ± 2	37.943 ± 11
SH652	18.216 ± 6	15.634 ± 4	38.335 ± 8	CF123	18.004 ± 10	15.529 ± 13	37.879 ± 15
268.5 m	18.209 ± 4	15.614 ± 10	38.320 ± 6		18.010 ± 9	15.535 ± 11	37.900 ± 12
SH652	18.098 ± 16	15.546 ± 9	38.001 ± 25	3/5000	18.026 ± 8	15.550 ± 6	37.939 ± 15

Samples dissolved in dilute HNO₃, purified by electrodeposition³⁵, and analysed (using single Re filament with silica gel and phosphoric acid) on the V.G. Isomass 54E mass spectrometer at SURRC. Measurements were corrected for mass discrimination by normalizing to the recommended values for the NBS 981 standard. Errors refer to least significant digits and are 2σ mean run precision. Long-term reproducibility is estimated at closer to ±0.1%. SH, surfacehole; UG, underground.

basement such as makes up the lower and middle crust in this area of Ireland²⁰, can be expected to have relatively unradiogenic Pb—the time-integrated effect of uranium depletion. Therefore a progression to less radiogenic values with time will be recorded in the lead isotope ratios of sulphides precipitated from the fluids which have extracted metals from progressively deeper levels in the crust.

The Navan orebody (Fig. 1), operated by Tara Mines Ltd, is one of several unmetamorphosed base-metal SEDEX deposits in Ireland which also includes Tynagh and Silvermines^{20–27}. Navan was chosen because of its size and because of the clear stratigraphic superposition of the lenses^{28,29}. There are five such lenses, numbers 2 and 3, usually classed as one unit (Fig. 1). The main Pb + Zn mineralization at Navan is hosted by Tournaianian bioclastic and oolitic limestones, micrites and minor sandstones. This sequence unconformably overlies Lower Palaeozoic shales and grits with Ordovician volcanic horizons. A syenite, thought to be of Silurian age occurs nearby. A metamorphic basement has been inferred at a depth of approximately 7 km beneath the orebody on the basis of geophysical data²⁰.

There is abundant evidence that the mineralization is sedimentary with early diagenetic additions and modifications^{29,30}. The stratigraphically lowest lens, number 5, was deposited first²⁸ and the main phase of mineralization terminated with deposition of

the stratigraphically highest number 1 lens. Some mineralization continued after the development of a submarine erosion surface with localized deposition of the pyritic Conglomerate Group Ore. The fact that mineralization extends into these Viséan sediments demonstrates the long-lived nature of this system (>10⁶ years). Galena samples were taken from all five lenses to provide a comprehensive study of Pb isotopic variation within this deposit. In addition, stratigraphically less well-defined samples from the associated exhalative ore at Tynagh and Silvermines were analysed to provide a comparison with both the Navan data and previously published data for Irish mineral deposits^{31–33}. All data and details of analytical techniques are presented in Table 1.

In Fig. 2 the ²⁰⁶Pb/²⁰⁴Pb ratios of the galena samples are shown as a function of stratigraphic lens position (hence time). The most radiogenic signature (²⁰⁶Pb/²⁰⁴Pb = 18.2) persists as a regular feature throughout the orebody (Fig. 2). Cross-cutting veins (not plotted) are in the range of the more radiogenic lead isotopic compositions observed. Although isotopic variation is apparent on a 'lens scale' the replicate analyses in Table 1 (from separate portions of the same hand specimen) are remarkably uniform.

The only model which specifically predicts a change with time to less radiogenic Pb isotopic compositions is that of downward

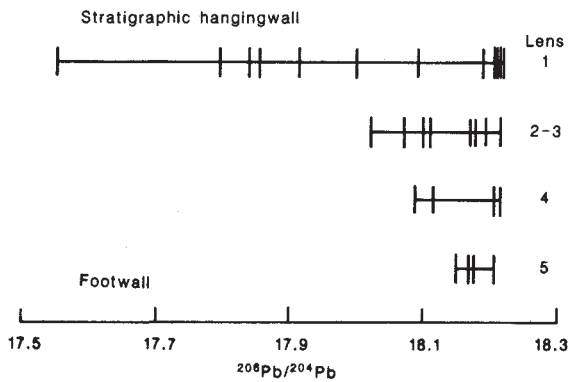


Fig. 2 Variation in $^{206}\text{Pb}/^{204}\text{Pb}$ in galenas with stratigraphic height in the Navan orebody.

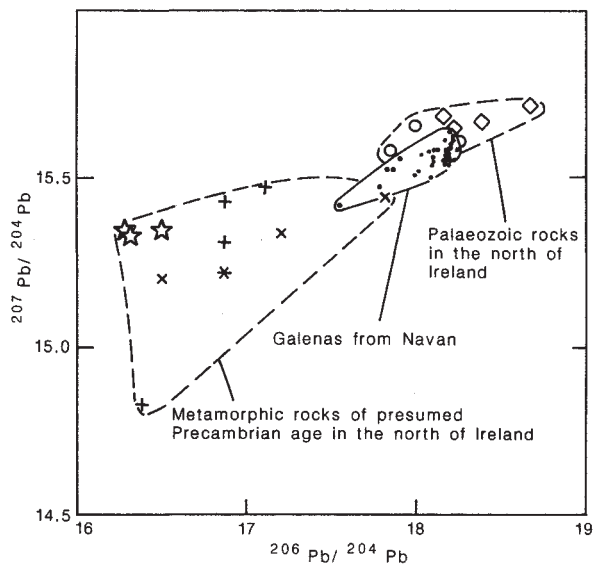


Fig. 3 Lead isotope data for Navan galenas compared with age corrected data (H. Mills, unpublished) for rock types in the north of Ireland. It is not thought that all these rock types underly Navan but the data nonetheless provide strong support for the model shown in Fig. 4. Newry data on feldspars. The remainder are on whole rocks. \star , Lewisian Inishtrahull; $+$ late Proterozoic-Ox Mountains; \times , late Proterozoic-Tyrone; $*$, granulite facies xenolith; \diamond , Lower Palaeozoic sediments—Navan; \circ , Newry granodiorite; \bullet , Navan galenas.

excavating convection cells. The fact that this prediction is fulfilled does not on its own rule out the relevance of other available models. However we doubt that they are significant for the following (and other¹⁶) reasons. There are striking differences between the kinds of results that have been observed in the lead-zinc deposits of the Mississippi Valley, that is, highly variable and radiogenic Pb, and those observed at Navan. Furthermore, Mississippi Valley type deposits *sensu stricto* commonly exhibit very large interdeposit differences in isotopic composition which does not fit with the relatively uniform, systematic lead isotopic compositions found across Ireland as a whole³¹⁻³³. A contemporary igneous source for the lead does not seem very reasonable since it does not explain the temporal variations in lead isotopic composition; but more importantly no Carboniferous igneous rocks³⁴ of significance are known in the vicinity. The fluid inclusion temperatures in Irish SEDEX deposits (estimated maximum of 250 °C) are too high to be easily reconciled with seismic pumping or basin brine expulsion models¹⁶. Finally, the fact that the Navan orebody was formed

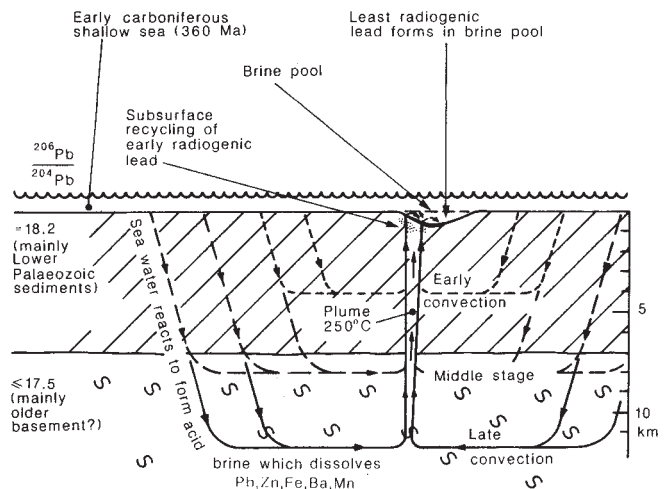


Fig. 4 Diagram illustrating the progress of a convection cell as it excavates downwards to tap older continental crust with less radiogenic lead which is transported upwards to form a giant exhalative orebody such as Navan.

early in the development of a sedimentary basin, is inconsistent with basin brine expulsion models.

The assumption that lead should be less radiogenic with depth in the crust is based on a generalized model that needs vindication by analysing local rock types. In Fig. 3 the lead isotope data for Navan mineralization is compared with unpublished data for a variety of potential type reservoirs in the northern half of Ireland. It can be seen that local Lower Palaeozoic sediments and 400 Myr old granites (as typified by the nearby Newry granodiorite) have lead isotopic compositions clustering around the radiogenic end of the spectrum of Navan results. In contrast, a variety of presumed Precambrian rocks in the northern half of Ireland have less radiogenic lead such that the Navan galenas span the two fields.

Based on this and geophysical²⁰ evidence a reasonable generalized 'lead isotopic stratigraphy' of the crust is suggested in Fig. 4 in which the Navan orebody is shown immediately underlain by Lower Palaeozoic sediments which in turn are underlain by a Precambrian basement at ~7 km depth. An explanation for the formation of the orebody in terms of deepening, expanding convection would be as follows. Carboniferous seawater penetrated the crust along fractures during periods of extension and the fluids spread out laterally at the point where penetration along fractures was no longer possible, that is, at the brittle/ductile transition. As the fluids circulated they were converted to acid brines which scavenged and mixed lead and other constituents from the uppermost crust. These buoyant hydrothermal fluids precipitated their constituents on the sea floor and within the sediments. The convection cell system advanced to greater depth with the brittle/ductile transition zone as the crust cooled.

The downward excavating convection model, on its own, does not explain the repeated tapping of lead with a radiogenic lead isotopic composition which persists as a signature throughout the evolution of the hydrothermal system. We consider that this lead is derived by the recycling in the uppermost crust of the lead homogenized and deposited during the formation of the lowest (and in fact the biggest) lens (lens number 5). Although we believe these processes are not unique to Navan, the time-resolved high-precision Pb isotope data are not yet available for other giant orebodies to determine whether this model of expanding convection cells is widely applicable.

We are indebted to Tara Mines for access to the Navan mine and drillcore, and to the chief geologist, Dermot Downing for his help. We would also like to thank our colleagues at Strathclyde University, SURRC and University of Michigan for

helpful comments and Alan Dickin and John Hutchinson for technical assistance. This work was carried out while two of us, H.M. and I.K.A. were in receipt of NERC grants. The isotope geology unit at SURRC is supported by NERC and the Scottish Universities.

Received 16 October 1986; accepted 26 February 1987.

- Halliday, A. N. & Mitchell, J. G. *Trans. R. Soc. Edin.* **74**, 1-14 (1983).
- Evans, A. M. in *Handbook of Stratiform and Stratiform Ore Deposits* Vol. 5 (ed. Wolf, K. H.) 231-255 (Elsevier, Amsterdam, 1976).
- Gustafson, L. B. & Williams, N. *Econ. Geol.* **76**, 139-178 (1981).
- Badham, J. P. N. *Trans. Instn Min. Metall.* **B90**, 70-76 (1981).
- McIntyre, D. G. in *Short Course in Sediment Hosted Lead-Zinc Deposits*: (ed. Sangster, D. E.) 141-174 (Mineral. Assoc. Canada, Victoria, 1983).
- Lydon, J. W. in *Short Course in Sediment Hosted Lead-Zinc Deposits*: (ed. Sangster, D. E.) 141-174 (Mineral. Assoc. Canada, Victoria, 1983).
- Morrissey, C. J., Davis, G. R. & Steed, G. M. *Trans. Instn. Min. Metall.* **B80**, 174-185 (1971).
- Evans, A. M. & Maroof, S. I. *Mining Mag.* **134**, 401-411 (1976).
- Campbell, F. A. & Ethier, V. G. *Miner. Deposita* **18**, 39-55 (1983).
- Finlow-Bates, T. *Geol. Jb.* **40**, 131-168 (1980).
- Russell, M. J. in *Implications of Continental Drift to the Earth Sciences* Vol. 1 (eds Tarling, D. H. & Runcorn, S. K.) 581-597 (Academic, London, 1973).
- Phillips, W. J. *Trans. Instn Min. Metall.* **B92**, 102 (1983).
- Gulson, B. L., Perkins, W. G. & Mizan, K. J. *Econ. Geol.* **78**, 1466-1504 (1983).
- Sibson, R. H., Moore, J. McM. & Rankin, A. H. *J. geol. Soc. Lond.* **131**, 653-659 (1975).
- Russell, M. J. *Trans. Instn Min. Metall.* **B87**, 168-171 (1978).
- Russell, M. J. in *Short Course in Sediment Hosted Lead-Zinc Deposits*: (ed. Sangster, D. E.) 251-282 (Mineral. Ass. Canada, Victoria, 1983).
- Due, B. R. & Delevaux, M. H. *Econ. Geol.* **67**, 409-425 (1972).
- Hart, S. R., Shimizu, N. & Sverjensky, D. A. *Econ. Geol.* **76**, 1873-1878 (1981).
- Doe, B. R. in *Lead Isotopes* 1-137 (Springer, New York, 1970).
- Brown, C. & Williams, B. J. *J. geol. Soc. Lond.* **142**, 1059-1075 (1985).
- Derry, D. R., Clark, G. R. & Gillatt, N. *Econ. Geol.* **60**, 1218-1237 (1965).
- Russell, J. M. *Trans. Instn Mon. Metall.* **B84**, 128-133 (1975).
- Boast, A. M., Coleman, M. L. & Halls, C. *Econ. Geol.* **76**, 27-55 (1981).
- Taylor, S. & Andrew, C. J. *Trans. Instn Min. Metall.* **B87**, 111-124 (1978).
- Taylor, S. *Econ. Geol.* **79**, 529-548 (1984).
- Banks, D. A. *Nature* **313**, 128-131 (1985).
- Boyce, A. J., Coleman, M. L. & Russell, M. J. *Nature* **306**, 545-550 (1983).
- Andrew, C. J. & Ashton, J. H. in *Mineral Exploration in Ireland, Progress and Development 1971-1981* (Irish Ass. for Economic Geologists, Dublin, 1982).
- Andrew, C. J. & Ashton, J. H. *Trans. Instn Min. Metall.* **B94**, 66-93 (1985).
- Anderson, I. K. *Abstr. Vol. Min. Dep. Study Group* (University of Strathclyde, 1985).
- Boast, A. M., Swainbank, I. G., Coleman, M. L. & Halls, C. *Trans. Instn. Min. Metall.* **B90**, 115-119 (1981).
- Caulfield, J. B., Lethusay, A. P. & Rye, D. M. in *Geology and Genesis of Mineral Deposits in Ireland* (eds Andrew, C. J. et al.) (Irish Ass. for Economic Geology, Dublin, 1986).
- O'Keefe, W. G. *Geology and Genesis of Mineral Deposits in Ireland* (eds Andrew, C. J. et al.) 617-624 (Irish Ass. for Economic Geology, Dublin, 1986).
- Smedley, P. L. *Earth planet. Sci. Lett.* **77**, 113-128 (1986).
- Arden, J. W. & Gale, N. H. *Analyt. Chem.* **46**, 2-9 (1974).

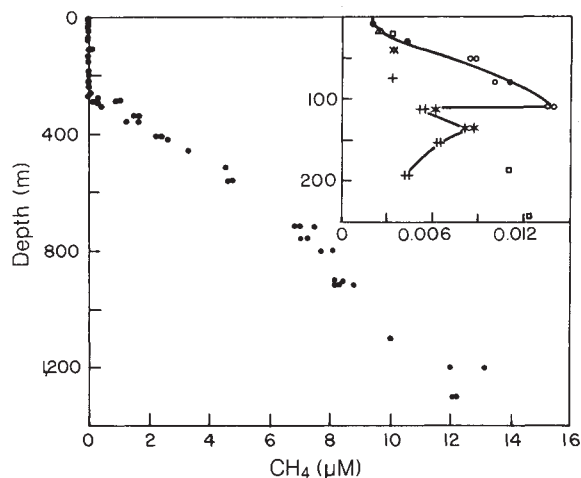


Fig. 1 Methane distribution in western Cariaco Basin during February and March 1986. Inset: expanded scale for surface layer. Different symbols represent different casts. Methane concentrations determined using vacuum extraction of dissolved gas from water sample²³ followed by injection of 100 to 500 μ l gas into Carle AGC 211 GC equipped with a flame ionization detector and 1/8-inch outer diameter, 5-foot stainless-steel column containing 60/80 mesh molecular sieve 5A. Precision and accuracy of concentration data are 3-5%. Equilibrium surface methane concentration $C_{eq} = \beta \chi_i^A (P - p^*)$ where C_{eq} is the equilibrium gas concentration, β , the Bunsen solubility coefficient²⁴, χ_i^A the partial pressure of gas in air ($= 1.7$ p.p.m.v.)^{8,9}, P , the barometric pressure and p^* , the water vapour pressure. Air-sea flux $= K_L (C_{meas} - C_{eq})$ (ref. 9) where $K_L = 3.8$ m per day is the liquid phase gas transfer coefficient at a wind speed of 8.5 m s⁻¹ and C_{meas} is *in situ* gas concentration at sea surface. Diffusional fluxes at concentration gradients $= K_v (\Delta C / \Delta z)$ where K_v is the vertical eddy diffusivity calculated from conductivity, temperature and depth (CTD) data as a function of the density gradient¹¹. $K_v = 0.20$ cm² s⁻¹ in the 50-80 m interval and 0.6 (from model⁷) or 0.78 (from density gradient) cm² s⁻¹ in the oxic/anoxic interface region (260-290 m). $\Delta C / \Delta z$ = the methane concentration gradient.

Methane oxidation and methane fluxes in the ocean surface layer and deep anoxic waters

B. B. Ward*, K. A. Kilpatrick*, P. C. Novelli† & M. I. Scranton†

* Institute of Marine Resources, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, USA

† Marine Science Research Center, State University of New York, Stony Brook, Long Island, New York 11794, USA

Methane is supersaturated in sea water, and is typically at its maximum concentration in near-surface waters, which could support a significant sea-air flux. The magnitude and variability of the flux depends on the mechanisms which produce and consume methane in sea water. Here, we compare measured biological oxidation rates of methane with the diffusional fluxes computed from concentration gradients in the surface layer of the ocean, and show that oxidation of methane in sea water is a mechanism which modulates the flux of methane from marine waters to the atmosphere. Methane fluxes and oxidation rates were investigated in surface waters, at the oxic/anoxic interface and in deep anoxic waters of the Cariaco Basin. Measured oxidation rates were

equivalent to 5% of the methane flux into oxygenated waters from the methane-rich deep waters and 10% of the flux into surface waters from the subsurface methane maximum. Thus oxidation was not sufficient to prevent a net sea-air flux. The total methane oxidation rate in the basin amounted to 1.5% of total primary production in the surface layer. Only a small fraction of oceanic primary production would be required to cycle through the methane pool to support the global atmospheric flux from the ocean¹.

A slight supersaturation of methane persists in sea water, even in well-oxygenated surface waters in the absence of known production mechanisms. Subsurface maxima are commonly observed²⁻⁵ but net fluxes between the ocean and the atmosphere of only several tens of nmol cm⁻² yr⁻¹ have been estimated. The diffusive flux away from the subsurface maximum is generally smaller than the flux at the air/sea interface, implying an *in situ* production term in the surface layer⁴. The shape of the subsurface maximum implies that the flux of methane to the atmosphere is controlled by *in situ* biological consumption processes.

In anoxic basins, there is an additional source of methane from anaerobic metabolism in the sediments. This is the case in the Cariaco Basin⁶; its oligotrophic surface waters cap a deep anoxic basin, separated from the Caribbean Sea by a sill at 150 m. The oxic/anoxic interface is generally found between 260 and 300 m, although the precise depth has varied over time^{6,7}. Below the interface, methane and sulphide accumulate to very high concentrations. Anoxic basins and sediments constitute large methane pools, which could contribute to the sea-air flux.