$^{40}Ar/^{39}Ar$ dating of marine ferromanganese crusts

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Ferromanganese crusts are now purported to provide potentially powerful proxy records of palaeoceanographic change. Hydrogenous crusts grow at rates of a few mm per million years. Unfortunately, it has proven extremely difficult to establish the exact growth rates and ages of different portions of these crusts. The most compelling data have been acquired using U-Th disequilibrium series and ^{10}Be geochronology. However these are only effective for the relatively recent past ($< 10^6$ years and $< 10^7$ years respectively). Longer term calibration has relied on chemical growth rate parameters such as Co chronometry, the basis for which would seem a little unreliable, and Sr isotope stratigraphy which is easily perturbed by diagenesis. Here we describe an attempt to use vacuum encapsulation $^{40}Ar/^{39}Ar$ geochronology.

K-Ar and $^{40}Ar/^{39}Ar$ dating techniques have been successfully applied to manganese oxide ore minerals from Precambrian manganese deposits (Lippolt and Hautmann, 1995) and authigenic precipitates in soil weathering profiles (Vasconcelos *et al.*, 1994; Ruffet *et al.*, 1996). These studies focused on K-rich hollandite group minerals such as cryptomelane ($K_{1-2}(Mn^{3+}, Mn^{4+})_8O_{16}nH_2O$) which were mechanically separated and purified of potentially contaminating phases (Lippolt and Hautmann, 1995; Ruffet, 1996). In some cases, single grains of cryptomelane were dated using laser ablation, and recoil loss of ^{39}Ar was an acknowledged difficulty. Therefore, we have attempted to extend the application of $^{40}Ar/^{39}Ar$ dating to marine hydrogenetic ferromanganese crusts, using vacuum encapsulation to capture the recoil fraction.

Samples

We analysed three well characterized crusts taken from the central Pacific, northwest Atlantic and central Indian Ocean. The Pacific crust, CD29-2 (16°42.4′ N, 168°14.2′ W), was raised from the Karin Ridge, at a depth of 2.3 km, in the Johnston Island Economic Exclusion Zone south of the Hawaiian Ridge. This crust grew at 2.1 mm/My as determined by ^{10}Be dating (Ling *et al*, 1997). The Atlantic crust, BM1969.05 (39°0′ N, 60°57′ W) was raised from the San Pablo seamount in the northwest Atlantic. Ages determined from analysis of $^{87}Sr/^{86}Sr$ indicate that the growth of BM1969.05 has ocurred in two stages: from 18.2 to 16.2 Ma the crust grew at a rate of 30 mm/My, whereas from 10.2 Ma to the the present, the crust grew at an average rate of 5.7mm/My (Burton *et al.*, 1997). However, the growth rate for BM1969.05 estimated by ^{10}Be dating is 1.62 mm/My (O'Nions *et al.*, in press). The third crust, SS663, was taken from a depth of 5.3 km in the central Indian Ocean at 13°S, 76°E. SS663 has grown at a rate of ~2.8mm/My as indicated by ^{10}Be dating (O'Nions *et al.*, in press).

Methods

We initially assumed that the dominant reservoirs of the potassium in the ferromanganese crusts were the hydrogenetic manganese oxide phases, vernadite and todorokite. We analysed the bulk crust material using the vacuum encapsulation method for $^{40}Ar/^{39}Ar$ analysis to prevent loss of ^{39}Ar in the recoil gas fraction. The analytical procedure is very similar to that described for $^{40}Ar/^{39}Ar$ analysis of clay minerals by Dong *et al.* (1997). Samples, ranging in mass from 0.1 to 8 mg, were irradiated for 6 or 20 hours. The samples were then step-heated using an Ar-laser, and the gas released from each step was analysed on our VG 1200S mass spectrometer operating in static mode. All data were corrected for machine mass discrimination, system blanks, irradiation-induced isotopic interferences with K, Ca and Cl, and reactor neutron flux gradients.

Results

The results for the 3 crusts vary significantly from each other, and in the case of the North Atlantic and

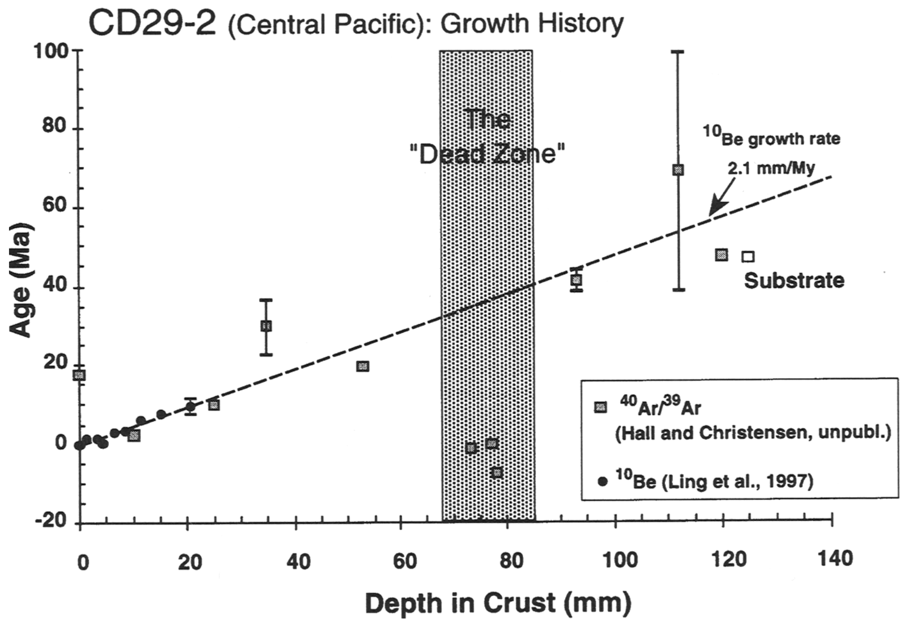

FIG. 1.

Indian Ocean crusts, do not provide any stratigraphically sensible age information. For the Central Pacific crust, CD29-2, there appears to be a general correlation between ages obtained from the $^{40}Ar/^{39}Ar$ technique and those that are predicted using the growth rate determined by the ^{10}Be method (Fig. 1). However, there is a section of CD29-2 at approximately 70–85 mm depth (here referred to as the 'dead zone') in which there is very little radiogenic Ar, thus producing near-zero ages. Excluding the zero-age interval, a linear regression through the dated sections of crust CD29-2 provides a growth rate of approximately 2.4 mm/My, in close agreement with the 2.1 mm/My rate determined from ^{10}Be dating. For the North Atlantic crust, ages obtained from 5 samples varied between 82–118 Ma, with no relation to stratigraphic position. Finally, for the Indian Ocean crust, ages ranged from 17–80 Ma, too old by a factor of ~4 relative to ages predicted by ^{10}Be growth rates.

SEM-EDS studies reveal that a primary reservoir of K in the crusts is dispersed in an even manner through the ferromanganese oxides. However, there are K rich spots that may represent detrital grains such as potassium feldspar. Alternatively they may indicate that the potassium was exchangeable with seawater, leading to redistribution. The older 'apparent' ages obtained for BM1969.05 and SS663 would be consistent with the former explanation because these samples were proximal to sources of old continental crust, thus resulting in apparent ages for the crusts that are slightly older than predicted using known growth rates. The dead zone of CD29-2 is perplexing, and may be due to loss of radiogenic Ar from the crust by diagenesis. Ultimately, the $^{40}Ar/^{39}Ar$ technique will be of limited use for dating ferromanganese crusts unless the detrital and authigenic minerals can be mechanically separated prior to irradiation.

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