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^{87}Sr/^{86}Sr chemostratigraphy of Neoproterozoic Dalradian carbonates below the Port Askaig Glaciogenic Formation, Scotland

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ABSTRACT

The Neoproterozoic–Cambrian Dalradian Supergroup of Scotland contains three glaciogenic sedimentary units, the Port Askaig Formation, the Stralinchy-Reelan Formation, and the Loch na Cille Boulder Bed, in ascending order. Although the idea, that relatively cold climates occurred during the latest Proterozoic, is widely accepted, the cause of the onset of glaciation is still controversial; we use new carbonate ^{87}Sr/^{86}Sr data to better constrain this environmental change. Some Dalradian limestones have high strontium contents (>1000 ppm), low manganese contents and Mn/Sr ratios (<0.2) and, according to their silica, aluminum and potassium contents and Rb/Sr ratios, they suffered insignificant contamination from siliciclastic minerals, thus they are suitable for estimating the ^{87}Sr/^{86}Sr values of paleoseawater in the Neoproterozoic. The ^{87}Sr/^{86}Sr values of limestones of the Islay Formation (*ca.* 0.7067), sampled on the island of Islay, are similar to the values of previous studies. However, the ^{87}Sr/^{86}Sr values of limestones just below the Port Askaig Formation (*ca.* 0.7064), collected on the island of Garbh Eileach, have the lowest values recorded in the Dalradian Supergroup. Comparing these ^{87}Sr/^{86}Sr values with coeval ^{87}Sr/^{86}Sr values of other regions in the world, such low ^{87}Sr/^{86}Sr (<0.7065) has only been reported from successions pre-dating the older Cryogenian (Sturtian) glaciation, which supports the idea that the Port Askaig Formation was deposited during the older Cryogenian glaciation. We have reconstructed the variations in the ^{i87}Sr/^{86}Sr ratio from the Tonian through the Cryogenian and Ediacaran to the earliest Cambrian. The results show that the ^{87}Sr/^{86}Sr ratio of seawater decreased just before the older Cryogenian glaciation, that it increased by two steps in the early and middle Ediacaran, and that there were at least two abrupt positive excursions in the middle Ediacaran and at the Precambrian–Cambrian boundary. The decline of the ^{87}Sr/^{86}Sr ratio of seawater just before the older Cryogenian Sturtian glaciation suggests that enhancement of weathering, related to break-up of the Rodinia supercontinent and continental flood basalt volcanism, was a likely driver for generating global cooling for the Snowball Earth conditions (Goddéris et al., 2003; Donnadieu et al., 2004).

1. Introduction

The Neoproterozoic period (1000–542 Ma) witnessed some of the most extreme climatic and biological changes in Earth history. Recent studies suggest that there were several glacial periods in the Neoproterozoic (Hoffman and Schrag, 2002; Kennedy et al., 1998; Fairchild and Kennedy, 2007); the older Cryogenian (Sturtian) and the younger Cryogenian (Marinoan) glaciations are widely accepted as the two largest. ^{87}Sr/^{86}Sr data are widely used to correlate Neoproterozoic sedimentary sequences and to decode surface environmental changes (Melezhik et al., 2001; Halverson et al., 2007; Sawaki et al., 2010). Based on a compilation of Sr isotope compositions through geologic time, Shields and Veizer (2002) suggested that the radiogenic Sr isotopic ratio suddenly increased in the Neoproterozoic compared with the period before, and they related the significant change in ^{87}Sr/^{86}Sr to the formation, break-up and dispersal of the supercontinent Rodinia. The ^{87}Sr/^{86}Sr composition of seawater mainly reflects a combination of less radiogenic strontium derived from hydrothermal alteration of oceanic crust and highly radiogenic input from continental weathering. Due

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to the large isotopic difference between these two main sources of strontium, the $^{87}Sr/^{86}Sr$ composition of seawater tracks long-term changes in the weathering of the earth's surface and the relative importance of the hydrothermal flux (e.g. Richter et al., 1992).

The Neoproterozoic to Cambrian Dalradian Supergroup of Scotland was deposited on the eastern margin of Laurentia and contains three glaciogenic successions, the Port Askaig Formation (Fm), the Stralinchy-Reelan Formation, and the Loch na Cille Boulder Bed, in ascending order (Harris et al., 1994; Stephenson and Gould, 1995; Condon and Prave, 2000; McCay et al., 2006). The Port Askaig Formation consists of over 700 m of diamictite, conglomerate, sandstone and minor carbonate, and is in the current spotlight due to the excellent preservation of its sedimentary structures. Although the age range of most Neoproterozoic successions is poorly constrained by radiometric or biostratigraphic dating, recent lithostratigraphy and chemostratigraphy have indicated that the Port Askaig Formation represents the older Cryogenian (Sturtian) glaciation (Prave, 1999; Condon and Prave, 2000; McCay et al., 2006; Prave et al., 2009). $^{87}Sr/^{86}Sr$ data are useful to constrain the age of such sedimentary sequences (Melezhik et al., 2001; Halverson et al., 2007). Brasier and Shields (2000) used the $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ of carbonate sediments beneath the Neoproterozoic Dalradian glaciogenic Port Askaig Formation to propose an older Cryogenian glacial age for these carbonates. Thereafter, Thomas et al. (2004), presenting new isotope geochemistry of limestones throughout the entire Neoproterozoic Dalradian, identified secular variations in their $^{87}Sr/^{86}Sr$ ratios.

This work presents new $^{87}Sr/^{86}Sr$ data from the Dalradian Supergroup. There is an unconformity between the Port Askaig Formation and underlying limestones on Islay (Brasier and Shields, 2000; Thomas et al., 2004). Therefore, we collected limestone samples on the island of Garbh Eileach (the largest of the Garvellach Islands), where the Port Askaig Formation rests conformably on limestones of the Islay Fm, and we studied the $^{87}Sr/^{86}Sr$ chemostratigraphy just below the Port Askaig Formation. Based on our new $^{87}Sr/^{86}Sr$ data and their comparison with global $^{87}Sr/^{86}Sr$ chemostratigraphy through the Neoproterozoic, we discuss the environmental changes before the older Cryogenian glaciation.

2. Geology of the Dalradian Supergroup

2.1. Geological setting

The Dalradian Supergroup of Scotland consists of siliciclastic and carbonate sedimentary rocks, together with subordinate volcanic rocks that were deposited on continental crust of the eastern margin of Laurentia from the Neoproterozoic to possibly the Middle Cambrian (Anderton, 1982, 1985, 1988; Harris et al., 1994; Cawood et al., 2003). The Dalradian is divided into four Groups (Figs. 1a, b and 2): Grampian (oldest), Appin, Argyll and Southern Highland (youngest). The Grampian Group is dominated by fluvial and marine siliciclastic sediments and a few limestones (Glover et al., 1995). The relationship between the base of the Grampian Group and gneissose metasedimentary rocks, which may constitute their basement, is unresolved (Smith et al., 1999). The Appin Group consists of a succession of siliciclastic rocks, quartzite and carbonate deposited in a shallow to deep marine environment. The Port Askaig Formation at the base of the Argyll Group mainly comprises a marine glaciogenic succession (Eyles and Eyles, 1983) that provides a detailed record of changing depositional conditions during a Neoproterozoic glaciation (Spencer, 1971). The diamictites are interbedded with sandstone, mudstone and conglomerate; the presence of giant cross-beds in the sandstone units indicates repeated ice margin advance and withdrawal, and the influence of strong tidal currents during the glaciation (Arnaud, 2004). The depositional environment of the Port Askaig Formation is hotly discussed (e.g. Benn and Prave, 2006) and summarized by Arnaud and Fairchild (in press). Deglaciation was followed by deposition of a thick siliciclastic-dominated sequence of marine deposits and subsequent dolostones: these rocks comprise the Bonahaven Formation. According to Brasier and Shields (2000), the Bonahaven Formation is a cap carbonate, but the presence of sandstones and mudstones below the Bonahaven dolostones indicates that the carbonate does not cap glacial rocks (Arnaud and Fairchild, in press). Although Brasier and Shields (2000) suggested that the negative $\delta^{13}C_{carb}$ values of the Bonahaven dolostones are correlated with those of another cap carbonate sequence (Dracoisen Formation, Svalbard), the negative signature suggests an early marine diagenetic origin (Fairchild and Kennedy, 2007).

Conglomerates at the bottom of the Easdale Subgroup of the Argyll Group may indicate a hiatus of deposition and/or an unconformity (Fig. 2). The middle to upper parts of the Argyll Group are dominated by coarse-grained siliciclastic rocks and limestones that were deposited in rapidly subsiding and relatively deep marine rift basins (Stephenson and Gould, 1995). Recently, McCay et al. (2006) reported a younger Cryogenian (Marinoan)-age glacial deposit in Ireland, the Stralinchy-Reelan Formation, which is composed of diamictite, and the overlying Cranford Limestone contains the characteristic features of a younger Cryogenian glacial-cap carbonate. This glacial-cap carbonate sequence in Ireland is correlated with the Easdale Subgroup in the Dalradian Supergroup (McCay et al., 2006; Prave et al., 2009). Continued subsidence led to deposition of thick turbiditic sandstones of the Southern Highland Group. The Loch na Cille Boulder Bed, the third glacial deposit, constitutes the lower part of this Group and is correlated with the Gaskiers (*ca.* 580 Ma; Bowring et al., 2003) glacial deposit (McCay et al., 2006). The Leny Limestone of Perthshire, which comprises thin-bedded turbiditic carbonates and contains the *Pagetides trilobite* fauna, probably belongs to the uppermost part of this Group (Tanner, 1995; Fletcher and Rushton, 2007).

Only four isotopic age data constrain the time of deposition of the Dalradian Supergroup. A U–Pb zircon and monazite age of a pegmatite in a shear zone that truncates the base of the Grampian Group gives minimum ages of 840 ± 11 Ma and 806 ± 3 Ma for the onset of Dalradian sedimentation (Highton et al., 1999; Noble et al., 1996). U–Pb zircon ages from a keratophyre and a felsic tuff in the Tayvallich Volcanic Fm. date the time of volcanism and sedimentation at the top of the Argyll Group at 595 ± 4 Ma and 601 ± 4 Ma, respectively (Halliday et al., 1989; Dempster et al., 2002). These data also provide a lower age limit for deposition of sedimentary rocks of the Argyll Group. Sediments of the Grampian, Appin and Argyll Groups were deposited in the period from 800 to 600 Ma.

2.2. Sampled carbonate units and localities

Winchester (1974) documented the metamorphic grade of the Grampian Highlands and showed that the lower-grade metamorphic facies is in the Southwestern Grampian Highlands (Fig. 1b). Because metamorphism and alteration are unfavorable for preservation of carbonate primary $^{87}Sr/^{86}Sr$, we collected samples in the better-preserved rocks on the Garbh Eileach and Islay Islands (Fig. 1), on both of which we produced a stratigraphic column (Figs. 3 and 4).

At Beannan Dubh on Islay (Fig. 1c) we collected rock samples from the Blair Atholl Subgroup and the Port Askaig Formation. The beds of carbonate and sandstone in this area strike NE–SW and dip NW (Fig. 1c). The Blair Atholl Subgroup comprises two carbonate units; the lower is the Ballygrant Fm and the upper is the Islay Fm (Fig. 3). The Ballygrant Fm crops out in the southeastern part of this area (Fig. 1c), and the contact between the