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Re–Os age constraints and new observations of Proterozoic glacial deposits in the Vazante Group, Brazil

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ABSTRACT

A new Re–Os radiometric age date for an organic-rich shale horizon from the Vazante Group in Brazil, coupled with geological observations, provide evidence for late Mesoproterozoic glacial episodes, conflicting with the general view of greenhouse conditions marked by a eustatic high stand at this time. Field observations of a reverse fault juxtaposing older Mesoproterozoic sedimentary rocks above younger Neoproterozoic strata provide a new stratigraphic framework and reconcile the apparent inversion of U–Pb detrital zircon ages through the succession. Combined, the geochronological, geochemical and stratigraphic evidence suggest that the Vazante Group sediments accumulated along a passive margin of the São Francisco craton and are correlative with the neighboring Paranoá Group. Biomarker, sulfur isotope and iron speciation analyses support the interpretation of a strongly stratified water column during post-glacial transgression and deposition of one of the bituminous shale horizons. The relationship of the glaciogenic Vazante Group to other late Mesoproterozoic successions, such as the non-glacial Atar Group in West Africa and Bylot Supergroup in arctic Canada, however, remains enigmatic.

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1. Introduction

The Precambrian geologic record contains evidence of widespread ice ages, including diamictite left behind by melting glaciers, capped by texturally and isotopically anomalous carbonate and organic-rich shale that accumulated in the wake of rising sea levels (Harland and Bidgood, 1959; Kaufman et al., 1991; Kirschvink, 1992; Kennedy, 1996; Hoffman et al., 1998; Schrag et al., 2002; Bekker et al., 2005). Existing age constraints suggest that these Precambrian ice ages were episodic rather than continuous, with a series of temporally discrete glaciation events occurring at the beginning and end of the Proterozoic Eon (*cf.* Kaufman et al., 1997; Kennedy et al., 1998; Walter et al., 2000; Kendall et al., 2004, 2006) but with little evidence of glaciation in the intervening billion years.

Due to the general lack of radiometric determinations on sedimentary successions, however, the absolute ages of many of the Proterozoic diamictites are poorly known. To advance understanding of the tempo and mode of these ancient ice ages, researchers have applied a geochronometer based on the radioactive decay of ^{187}Re to ^{187}Os, most commonly on samples of organic-rich shale preserved in drill cores (Kendall et al., 2004, 2006; Azmy et al., 2008; Rooney et al., 2010) or syn-depositional sulfide grains (Hannah et al., 2004). Published results for Neoproterozoic (1.0–0.542 Ga) successions support the view that the Sturtian and Marinoan glacial epochs represented multiple discrete ice ages over a protracted time frame (*cf.* Kaufman et al., 1997). Contrary to expectations, a Re–Os study of a dropstone-laden shale horizon from the Vazante Group in south-central Brazil (Azmy et al., 2008) indicated a late Mesoproterozoic age – a time previously believed to have been ice free.

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In this paper, we re-evaluate the stratigraphic position of this shale, which was previously interpreted to be syn-glacial in origin (Olcott et al., 2005) and support the Mesoproterozoic age with new Re–Os work from a second shale horizon unrelated to glacial deposits, as well as identify a thrust fault lower in the Vazante Group that juxtaposes older Mesoproterozoic strata above younger glaciogenic sedimentary rocks of Neoproterozoic age. Detrital zircon U–Pb constraints for the Vazante Group (Rodrigues et al., 2012), coupled with carbon and strontium isotope data and paleontological evidence, are consistent with the stratigraphic inversion and our Re–Os age determinations.

2. Geologic and geochronologic background

The Vazante Group is a sedimentary succession that occurs in wide swaths atop the eastern part of the Brasília Fold Belt (BFB) on the western margin of the São Francisco craton throughout Minas Gerais, Brazil (Fig. 1). Surface outcrops are strongly weathered and the succession has been exposed to sub-greenschist facies metamorphism (Babinski et al., 2005; Azmy et al., 2008), but well preserved carbonate and organic-rich shale are available in drill core. Fig. 2 shows a generalized stratigraphy of the Vazante Group, including three potential glacial horizons, as well as the reverse fault located near the town of Lagamar (Pinho and Dardenne, 1994), which resulted in older strata of the Vazante Group – including the shale horizons studied here – to overly younger sedimentary rocks (see Section 5.1 for further details and implications). The basal Vazante diamictite (St. Antônio do Bonito Formation) has long been interpreted as glacial in origin based on the presence of faceted and striated cobbles of mixed lithology, including basement clasts, floating in a mudstone matrix (Dardenne, 2000). The two upper Vazante Group diamictites at the base of the Morro do Calcário and Lapa formations are characterized by carbonate breccia or laminated shale disrupted by carbonate dropstones. Further evidence for a glacial origin for the two upper Vazante diamictites includes: (1) their widespread distribution across the basin; (2) the observation that cobbles and boulders in the Morro do Calcário (previously attributed to the Serra do Poço Verde Formation) are both rounded and angular, with the rounded stones often faceted (Fig. 3A and B); (3) the thick black Morro do Calcário shale contains glendonite, a pseudomorph of ikaite, a carbonate mineral that forms in organic-rich sediment at temperatures between −1.9 and 7 °C (*cf.* Olcott et al., 2005); (4) the uppermost strata of the Lapa diamictite are Fe-oxide cemented with local accumulations of iron-formation (*cf.* Derry et al., 1992; Kaufman et al., 1997; Hoffman et al., 1998); and (5) the carbonates and marl overlying both diamictites preserve negative $\delta^{13}C$ excursions typical of post-glacial cap carbonates (Azmy et al., 2001, 2006; Brody et al., 2004).

The three shale horizons sampled for Re–Os analysis in this study were from, in ascending order, the pre-glacial Serra do Garrote Formation and the post-glacial Morro do Calcário and Lapa formations. The Serra do Garrote Formation consists of dark gray shale hundreds of meters thick that has been metamorphosed to a greenish slate in some areas; the shale can be carbonaceous and/or pyrite bearing (Dardenne, 2000). The Morro do Calcário and Lapa formations are both composed of laminated shale and dolostone, which contain intermittent ice-rafted debris and based on core observations are each several hundred meters thick (Dardenne, 2000). The true thickness of these units, however, is difficult to ascertain insofar as outcrops are discontinuous and coupled with the likelihood of tectonic repetition of strata due to thrust faulting. The Morro do Calcário and Lapa formations accumulated during post-glacial transgression over sub-glacial valleys largely filled with carbonate breccia. Sub-glacial unconformities cut through underlying carbonate platform deposits of the Serra do Poço Verde and Morro do Calcário formations (indicated by the heavier formation-boundary lines in Fig. 2); in some cores it appears that the two upper Vazante Group diamictites are in direct contact while in others they are separated by a variety of bedded lithologies.

The age of the Vazante Group is controversial. Cloud and Dardenne (1973) argued that the presence of the stromatolite *Conophyton metula Kirichenko* (Fig. 3C) near the base of the Lagamar Formation suggests an age ranging between 1350 and 950 Ma. Stromatolite biostratigraphy, however, is poorly constrained and competing tectonic models suggest a Neoproterozoic initiation of Vazante Group sedimentation either in a rapidly subsiding foreland basin associated with the Brasíliano collision (*ca.* 790 Ma; Dardenne, 2000) or along a passive continental margin during supercontinent breakup (*ca.* 900 Ma; Pimentel et al., 2001). Whole rock Rb–Sr data for a Vazante Group shale yielded an isochron age of ~600 Ma, but this age likely represents a date related to Brasíliano metamorphism (Amaral and Kawashita, 1967). A Neoproterozoic age for the upper Vazante Group was suggested based on a comparison of time-series isotope trends (Azmy et al., 2001), although an alternative interpretation of these variations suggested an older potential age for the succession (Misi et al., 2007). Most recently, Re–Os dates of 993 ± 46 and 1100 ± 77 Ma (excluding Re- and Os-poor samples) were determined from a dropstone-laden shale in the Vazante Group previously believed to be part of the Lapa Formation (Azmy et al., 2008) but here is assigned to the Morro do Calcário Formation (see below).

3. Methods

All samples were taken from two pristine drill cores provided by Votorantim Metais. For Re–Os analysis, samples were selected from the Serra do Garrote Formation in drill hole 134-86, from roughly coeval horizons of the Morro do Calcário Formation in drill holes 42-88 and 134-86 and from the Lapa Formation in drill hole 134-86. The upper two shale horizons in core 134-86 are separated by a thick interval of carbonate breccia, quartzite and iron-cemented diamictite (Brody et al., 2004). In 2009, we re-examined this core and concluded that the shale horizon Azmy et al. (2008) studied from drill hole MASW-01 belonged to the Morro do Calcário Formation, rather than the Lapa Formation as previously discussed.

3.1. Re/Os

The Re–Os system can provide precise depositional ages for organic-rich shale because these facies are often deposited in anoxic environments where Re and, to a lesser extent, Os may be sequestered from seawater in their reduced states and incorporated into organic matter (Ravizza and Turekian, 1989; Cohen et al., 1999; Selby and Creaser, 2003; Kendall et al., 2004). Once incorporated in the sediment, ^{187}Re undergoes beta decay to ^{187}Os with a half-life of approximately ~42 Ga. With the assumption that all of the shale samples in a suite have the same initial osmium isotopic composition (from coeval seawater) and a wide range in parent:daughter ratios, it is possible to generate an isochron, which yields the age of incorporation of Re and Os into the system and, hence, of deposition. Since shale facies contain both hydrogenous and terrigenous components, it is necessary to digest the samples with a less-aggressive medium, such as Cr^{VI}-H_2SO_4, which preferentially attacks the organic component while leaving the detrital quartz and feldspar largely intact (Selby and Creaser, 2003).

Approximately 50 mg of powdered whole rock was accurately weighed along with a known quantity of a ^{190}Os–^{185}Re spike and Cr^{VI}-H_2SO_4 digestion solution (Selby and Creaser, 2003) and transferred to frozen Carius tubes that were chilled using a mixture of