Stable Isotopic ($\delta^{13}C$ and $\delta^{18}O$) Signatures of Biogenic Calcretes Marking Discontinuity Surfaces: A Case Study from Upper Cretaceous Carbonates of Central Dalmatia and Eastern Istria, Croatia

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Stable isotopes of carbon as an invaluable stratigraphic tool: An example from the Cambrian of the northern Appalachians, USA

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ABSTRACT

This study illustrates the usefulness of carbon isotopes in stratigraphic interpretations of poorly fossiliferous strata beyond the resolution possible by biostratigraphy. The Upper Cambrian strata of the lower Gorge Formation in northwestern Vermont have been interpreted as highly condensed continental-slope deposits with a hiatus bracketed by the trilobite fauna of the *Dunderbergia* zone (Steptoean) and the *Saukia* zone (upper Sunwaptan). This interpretation was based on information from two thin fossiliferous intervals, the occurrence of one of them being unconfirmed in a recent study. Carbon isotopes provide a means for testing this interpretation because marine carbonate rocks deposited during the Steptoean Age of the Late Cambrian record a large, global, positive carbon isotope excursion ($\delta^{13}C$ values of up to +5‰ relative to the Vienna Peedee belemnite standard). If the proposed age for the lowermost Gorge Formation is correct, these strata should record the start of the excursion, and the hiatus should produce an abrupt termination in the record of the excursion near maximum values. The determined $\delta^{13}C$ values (−0.57‰ to +0.39‰) indicate that the excursion is not recorded at this locality. The results question the age for these strata and suggest that the hiatus is greater than previously recognized, encompassing most of the Steptoean. This major sedimentary hiatus lends supporting evidence for a significant eustatic or pan-Laurentian sea-level event during the Steptoean perturbation in the global cycling of carbon.

Keywords: Cambrian, carbon isotopes, Gorge Formation, stratigraphy, Vermont.

INTRODUCTION

High-resolution stratigraphy of Upper Cambrian strata throughout the Appalachians is hindered by dense vegetation and thick soil cover that limit the exposure to small, isolated and widely spaced outcrops. Strata at these outcrops are commonly poorly fossiliferous, highly dolomitized, tectonically deformed, and metamorphosed. Characteristic geochemical signatures, especially stable isotopes of carbon, are promising tools in regional stratigraphic studies of these strata. A large, global, positive carbon isotope excursion ($\delta^{13}C$ values of up to +5‰ relative to Vienna Peedee belemnite standard [VPDB]), recorded in marine carbonate rocks deposited during the Steptoean Age of the Late Cambrian, provides a useful chemostratigraphic marker. This carbon isotope excursion has been documented in Steptoean strata from the United States, Australia, China, and Kazakhstan (Brasier, 1993; Glumac and Walker, 1998; Saltzman et al., 1998, 2000). The beginning of the excursion is coincident with the base of the Steptoean Stage and the *Aphelaspis* zone. The maximum excursion in the late Steptoean corresponds with the Dresbachian-Franconian Stage boundary and the Sauk II–Sauk III sequence boundary. The excursion ended during the *Elvinia* zone near the end of the Steptoean.

The goal of this study is to use carbon isotopes to improve the age resolution of an interval that was dated previously only with low-resolution biostratigraphic indicators, and to contribute new stratigraphic information on a significant Cambrian time interval (Steptoean) during which the global carbon cycle was severely perturbed. Carbon isotope stratigraphy was applied to a poorly fossiliferous continental-slope succession of the lower Gorge Formation at its type locality, Highgate Gorge in northwestern Vermont of the northern Appalachians (see Landing, 1983, for detailed locality map). A comprehensive biostratigraphic study of these strata by Landing (1983, p. 1157) suggested ''a probable cryptic unconformity resulting either from development of a truncation surface, nondeposition, or sediment bypassing has resulted in apparent loss of any record of the uppermost Dresbachian, Franconian, and lower Trempealeauan Stages'' and that the oldest, nonfossiliferous strata of the Gorge Formation belong to the *Crepicephalus*(?) and *Aphelaspis* zones of the Dresbachian (Fig. 1). The relationship between these traditional stage terms of the Upper Cambrian (Dresbachian, Franconian, and Trempealeauan) and the modern stage terms (Marjuman, Steptoean, and Sunwaptan) is indicated in Figure 1. The traditional stage names are used only when necessary for comparison with previous biostratigraphic interpretations. If these interpretations are correct, the strata of the lower Gorge Formation should record the start of the Steptoean carbon isotope excursion, which should terminate abruptly near its maximum because of the stratigraphic gap (Fig. 1). This study aims at determining whether this characteristic carbon isotope signature is present in the Gorge Formation so that the age interpretation of these strata can be improved. The carbon isotope record could be subsequently used as a stratigraphic marker throughout and beyond the northern Appalachians for correlation of Upper Cambrian carbonate rocks that lack fossils and cannot be dated biostratigraphically.

GEOLOGIC SETTING

Cambrian strata in Vermont are a part of the lower Paleozoic passive-margin sedimentary succession of eastern (present-day) Laurentia. These strata form an eastern basinal succession and a western shelf succession (Mehrtens and Hadley, 1995). The Gorge Formation is a part of the eastern basinal succession dominated by slates and carbonate clast conglomerates exposed east of the Champlain thrust complex in northwestern Vermont (Cady, 1945; Landing, 1983). In western-central Vermont these deposits grade into coeval platform carbonates of the western shelf succession (Rodgers, 1968).

A >150-m-thick Cambrian-Ordovician section of the Gorge Formation and the overlying Highgate Formation is well exposed along the Missisquoi River at Highgate Gorge in northwestern Vermont (Landing, 1983). This study focused on the 22-m-thick basal portion of the section, which corresponds to units 1–5 of the lower Gorge Formation from Landing (1983). Unit 1 consists of massive (0.5–1.0 m thick), lenticular beds of dolostone-clast conglomerates with a poorly sorted, coarse-grained dolomitic quartz arenite and sandy dolostone matrix (Fig. 1). The dolostone clasts are subrounded to subangular, range from 0.5 to 10 cm in diameter, and are composed mainly of medium crystalline dolomite. Surrounding these clasts is medium crystalline to coarsely crystalline dolomite with common detrital quartz grains. Thinly bedded, dark gray, dolomitic shale layers are interbedded with the dolostone-clast conglomerates of unit 1 (Fig. 1). Finely crystalline to medium crystalline dolomite is present in these shale layers. Units 2–4 consist of dark gray, 2–20-cm-thick layers of sandy sucrosic

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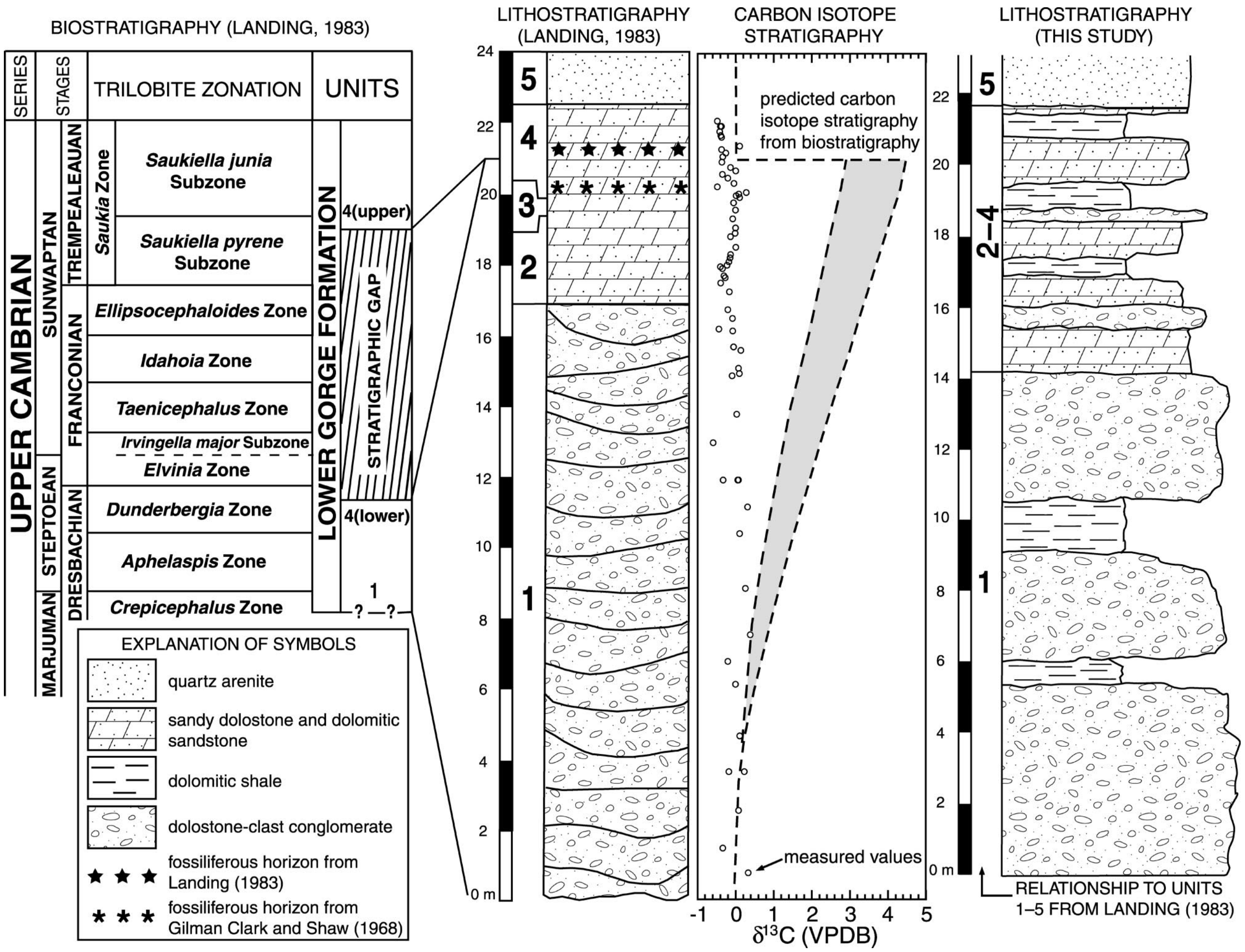

Figure 1. Relationships among biostratigraphy, lithostratigraphy, predicted carbon isotope stratigraphy, and measured carbon isotope values for lower Gorge Formation strata. VPDB—Vienna Peedee belemnite.

dolostones and dolomitic quartz arenites, overlain by a light buff, massive quartz arenite of unit 5 (Landing, 1983; Fig. 1). The dolostone layers have common detrital quartz in a mosaic of finely to coarsely crystalline dolomite. The strata composing units 2–4 are interbedded with several dolomitic shale and dolostone-clast conglomerate intervals compositionally similar to those from unit 1 (Fig. 1).

The Gorge Formation deposits are interpreted as a highly condensed continental-slope succession of thin-bedded carbonate-shale rhythmites alternating with thick-bedded debris-flow conglomerates (Landing, 1983; Taylor et al., 1991). The sediment was transported from shallower upper slope and outer carbonate-platform environments, located to the south and southwest in western-central Vermont, and deposited in a water depth of ~90 m (Landing, 1983; Taylor et al., 1991). Lenticular conglomerate layers at the base of the section represent amalgamated debris flows deposited as a proximal toe-of-slope sediment-apron complex (Landing, 1983; Taylor et al., 1991). The overlying thin-bedded sandy dolostones and black lime mudstones were deposited by turbidity currents in a more distal environment (Landing, 1983). Physical evidence for sedimentary condensation in the Gorge Formation includes stratigraphic cutouts and truncation surfaces at the base of debris aprons (Landing, 1983). In addition, biostratigraphic data suggest that a thin interval of sandy dolostones from unit 4 has been profoundly condensed: Landing (1983) documented upper Sunwaptan (middle Trempealeauan) fauna 1.25 m above the base of unit 4, but did not relocate the Steptoean *Dunderbergia* zone fauna described by Gilman Clark and Shaw (1968) in the lower part of unit 4 (Fig. 1). This evidence was combined to infer that this stratigraphic interval may contain one or more cryptic disconformities and may represent a period of nondeposition encompassing the entire Franconian through the early Trempealeauan (the late Steptoean through the middle Sunwaptan; Fig. 1; Landing, 1983).

STABLE ISOTOPE ANALYSIS

Methods

Samples for stable isotope analysis represent homogeneous dolomite matrix material drilled from polished and stained thin-section billets and slabs by using a microscope-mounted microdrill[1]. The powdered samples were roasted at 380 °C in a vacuum for 1 h to remove all volatile contaminants. The samples were reacted at 76 ± 2 °C with 3 drops of anhydrous phosphoric acid (H_3PO_4) for 12 min in a Finnigan Kiel preparation device coupled directly to the inlet of a Finnigan MAT 251 triple-collector isotope-ratio mass spectrometer at the Stable Isotope Laboratory at the University of Michigan. The determined $\delta^{13}C$ and $\delta^{18}O$ values are reported in per mil relative to the VPDB standard. The measured precision was maintained at better than 0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$.

Results

The measured $\delta^{13}C$ values have a very narrow range, from −0.57‰ to +0.39‰ (Fig. 1). The $\delta^{18}O$ values range from −6.27‰ to −3.54‰ and show no correlation with the $\delta^{13}C$ values (Fig. 2).

[1]GSA Data Repository item 2002057, Table DR-1, Sample description and $\delta^{13}C$ and $\delta^{18}O$ data, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2002.htm.

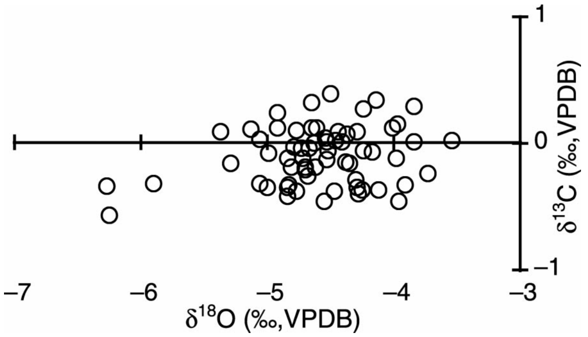

Figure 2. Relationship between $\delta^{18}O$ and $\delta^{13}C$ values. VPDB—Vienna Peedee belemnite.

DISCUSSION

Steptoean Carbon Isotope Record

The determined $\delta^{13}C$ values indicate that the positive carbon isotope excursion is not recorded in the strata of the lower Gorge Formation at Highgate Gorge (Fig. 1). If carbonate deposits of Steptoean age were present in this continental-slope succession, they would most likely have elevated $\delta^{13}C$ values because (1) the Steptoean carbon isotope excursion is global in scope, (2) the nature of the carbon isotope system allows the preservation of primary or close to primary signatures, and (3) the Steptoean excursion is readily recorded in allochthonous deep-water carbonate deposits.

Glumac and Walker (1998) documented the Steptoean positive carbon isotope excursion in the eastern United States (the southern Appalachians of Tennessee). Brasier (1993) and Saltzman et al. (1998, 2000) examined the record of the excursion in the western United States (the Great Basin area), China, Kazakhstan, and Australia. These studies indicate that the excursion is a widespread and most likely global phenomenon. The magnitude of this excursion (+5‰) is greater than the documented variation of carbon isotope compositions for modern oceans (−0.5‰ to +2.0‰; Kroopnick, 1985), and positive excursions of this scale are sufficiently uncommon to be readily identified in the geologic record (Saltzman et al., 2000). Therefore, this carbon isotope excursion is an invaluable stratigraphic marker for intrabasinal and interbasinal correlation of Steptoean strata in the absence of biostratigraphic indicators.

Massive alteration of $\delta^{13}C$ values of carbonate phases during diagenesis is hindered by small concentrations of carbon in the diagenetic fluids. Carbonate $\delta^{13}C$ values can be modified only in very open diagenetic systems (high fluid/rock ratio) and in the presence of brines with elevated levels of total dissolved carbon (Banner and Hanson, 1990). Lack of systematic covariance between $\delta^{13}C$ and $\delta^{18}O$ values is commonly cited as evidence that the $\delta^{13}C$ signature is not strongly influenced by diagenetic alterations (Fig. 2). The record of the Steptoean carbon isotope excursion is preserved in extensively altered rocks that consist of fabric-obliterated, coarsely crystalline dolomite and that interacted with Mississippi Valley–type hydrothermal brines (Glumac, 1997; Glumac and Walker, 1998), suggesting that carbon isotope stratigraphy can be applied to highly dolomitized, deformed, and even metamorphosed strata.

Saltzman et al. (2000) documented the Steptoean positive carbon isotope excursion in deep-water carbonate deposits from Australia, Kazakhstan, and China. In Australia, the excursion is recorded in finely laminated, organic-rich pyritic deposits from a deep-water intracratonic basin. Fine-grained, dark colored argillaceous limestone and carbonate gravity-flow deposits from a submarine-fan environment on the flank of a seamount record the Steptoean excursion in Kazakhstan. The record of the excursion in China comes from slope deposits at a transition between the shallow-water carbonate platform and the deep-basinal setting. The slope deposits consist of rhythmically bedded argillaceous limestones and calcareous shales with minor dolomitic limestones.

Interbedded with these deposits are limestone-clast breccia beds interpreted as debris flows produced by episodic slumping of the upper slope and carbonate-platform margin (Saltzman et al., 2000). These deposits share many characteristics with the continental-slope deposits of the Gorge Formation in Vermont, which consist of allochthonous sediment transported from shallower upper slope and outer platform environments (Landing, 1983; Taylor et al., 1991). Dolomitization of allochthonous fine-grained carbonate sediment can account for the abundant homogeneous dolomitic matrix in the Gorge Formation strata. Therefore, carbonate deposits from the Gorge Formation would have a high potential to record elevated $\delta^{13}C$ values if they were composed of sediment of Steptoean age.

Stratigraphy of the Gorge Formation

Biostratigraphic interpretations of the lower Gorge Formation (Landing, 1983) suggest that $\delta^{13}C$ values should record an increase above background range (−1‰ to +1‰) at the beginning of the *Aphelaspis* zone (Fig. 1). The proposed stratigraphic gap should result in the record of the excursion to be abruptly terminated near the maximum $\delta^{13}C$ values (+4‰ to +5‰), which were reached in the late Steptoean (or at the Dresbachian-Franconian boundary; Fig. 1). The overlying upper Sunwaptan strata should have postexcursion $\delta^{13}C$ values (~0‰; Fig. 1). That the strata of the lowermost Gorge Formation do not record the carbon isotope excursion leads to questions concerning their proposed Steptoean age (Fig. 1).

The carbon isotope data support a postexcursion (late Sunwaptan) age for strata from the upper part of unit 4 with *Saukiella pyrene* or lower *Saukiella junia* subzone faunas of the *Saukia* zone (Fig. 1; Landing, 1983). Sunwaptan and younger fossils documented higher up in the section confirm the latest Cambrian and earliest Ordovician age for strata from the Gorge Formation and the overlying Highgate Formation at Highgate Gorge (Landing, 1983; Taylor et al., 1991). The results of carbon isotope analysis, however, are not in agreement with the Steptoean age for the strata from the lower part of unit 4 with presumable *Dunderbergia* zone trilobites (Gilman Clark and Shaw, 1968). The questionable late Marjuman and Steptoean age (*Crepicephalus* to *Dunderbergia* zone) interpretation for the lowermost Gorge Formation (Fig. 1; Landing, 1983) was based on the work of Gilman Clark and Shaw (1968). This work was evaluated by A.R. Palmer, F. Rasetti, and J.W. Wilson, who ''called attention to the apparent mixing of incongruent elements'' (Gilman Clark and Shaw, 1968, p. 382) in this part of the succession, but did not question the *Dunderbergia* zone affinity of the fossils. Therefore, it is presumed that Gilman Clark and Shaw's (1968) identifications of the only late *Dunderbergia* zone fauna in Vermont were correct, but that the fossiliferous horizon must have been thin and not laterally extensive. There have been no typical Franconian trilobites documented from Vermont, and prior to Gilman Clark and Shaw's (1968) findings, the entire Gorge Formation was considered to be late Sunwaptan (Trempealeauan) in age, unconformably overlying the Rockledge Breccia with the *Crepicephalus* zone trilobites (Raymond, 1937; Shaw, 1951). No actual unconformity has been observed in the field, but a considerable hiatus spanning the entire Franconian (late Steptoean and early Sunwaptan) was proposed for the northern Appalachians (Wilson, 1952).

The carbon isotope results cannot directly discriminate between the post-*Elvinia* (Sunwaptan) and the pre-*Aphelaspis* (Marjuman) age interpretations for the lowermost Gorge Formation. Even though mixing of noncontemporary faunas can occur by slope-sedimentation processes in continental-margin and basinal settings (Taylor et al., 1991), the Sunwaptan age for the lowermost Gorge Formation is unlikely because the entire Franconian is represented by a hiatus and the *Dun-*

derbergia zone fauna was documented more than 20 m above the base of the section, from argillaceous or silty, finely laminated carbonate deposits (Fig. 1; Gilman Clark and Shaw, 1968). Therefore, the lowermost Gorge Formation is likely Marjuman in age. The occurrence of one thin horizon with *Dunderbergia* zone fossils (Gilman Clark and Shaw, 1968) and the complete absence of elevated $\delta^{13}C$ values in the lower Gorge Formation (Fig. 1) indicate that there was very little (if any) carbonate sediment deposited during the Steptoean.

Significance of the Results

This study illustrates the usefulness of carbon isotopes in stratigraphic interpretations beyond the level resolvable by biostratigraphy and encourages the application of chemostratigraphy to scarcely fossiliferous Upper Cambrian strata throughout and beyond the Appalachian basin. The carbon isotope data suggest that the stratigraphic gap in the lower Gorge Formation, recognized by Landing (1983), should encompass most of the *Dunderbergia* and *Aphelaspis* zones, and not just the late *Dunderbergia* zone (Fig. 1). The results support the interpretation that this continental-slope package is highly condensed and indicate that the stratigraphic gap represents a longer time period than previously recognized. The stratigraphic condensation likely occurred during a sea-level fall, as sediment bypassed the shelf and portions of the continental slope. This interpretation is consistent with the occurrence of the widespread Steptoean (or Dresbachian-Franconian) hiatus on the Laurentian craton, which marks the Sauk II–Sauk III sequence boundary (Lochman-Balk, 1971; Palmer, 1981). The Steptoean carbon isotope excursion has been documented in the correlative conformity or sequence boundary-zone intervals from Laurentian passive margin successions (Glumac and Walker, 1998; Saltzman et al., 1998). The results presented here provide new information about the location and nature of this important sequence stratigraphic interval in the continental-slope succession of the northern Appalachians and can serve as a base for high-resolution correlation with coeval intervals elsewhere. The evidence presented also suggests that the large Steptoean perturbation in the global cycling of carbon occurred during a sea-level fall, which likely represents a significant eustatic or pan-Laurentian event.

CONCLUSIONS

A detailed carbon isotope analysis of the lowermost Gorge Formation at Highgate Gorge in northwestern Vermont (northern Appalachians) determined that these strata do not contain a record of the Steptoean positive carbon isotope excursion. This result leads to questions concerning the Steptoean age (*Aphelaspis* to *Dunderbergia* zone) for these strata and suggests that this Upper Cambrian continental-slope succession is even more condensed than previously recognized, with a stratigraphic gap spanning most of the Steptoean (post-*Crepicephalus* zone). This major sedimentary hiatus supports the interpretation that the Steptoean perturbation in the global carbon cycle occurred during a significant sea-level fall.

ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through a grant to Glumac. A Sigma Xi grant-in-aid of research to Spivak-Birndorf provided additional funds. We thank Kyger C Lohmann and Lora Wingate, University of Michigan, for their help with stable isotope analysis. Tony Caldanaro assisted with thin-section preparation and Sooz DeYoung assisted with field work. Thoughtful reviews by Ed Landing and Matthew R. Saltzman improved the manuscript.

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Manuscript received October 22, 2001
Revised manuscript received February 25, 2002
Manuscript accepted March 6, 2002

Printed in USA