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Earth and Planetary Science Letters 147 (1997) E1–E7

EPSL

Express Letter

The Vendian–Cambrian $\delta^{13}C$ record, North Iran: evidence for overturning of the ocean before the Cambrian Explosion

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Received 1 October 1996; accepted 17 January 1997

Abstract

Continuous fossiliferous successions across the Precambrian/Cambrian (PC/C) boundary in the Elburz Mountains of Northern Iran show a remarkable negative $\delta^{13}C$ excursion just below the PC/C boundary. High concentrations of manganese, phosphorus, barium, and high abundances of fossil phytoplankton, and black shale coincide with the excursion. Worldwide stratigraphic correlation shows that the isotopic anomaly is a global event. The initial Metazoan diversification, coupled with ^{13}C enrichment, occurs stratigraphically just above the excursion.

We propose the following scenario for oceanic environmental changes before the Cambrian Faunal Explosion based on new data from Iran: A global warm climate following the last Precambrian glaciation resulted in a generally stagnant oceanic condition, so that surface water was oxic; deep water was dysoxic, depleted in ^{13}C, and enriched in nutrients. Massive upwelling of deep water (vertical advection of nutrients and ^{13}C-depleted CO_2) caused enhanced phytoplankton productivity and a sharp drop in $\delta^{13}C$ in shallow water carbonate and organic carbon. We conclude that latest Cryptozoic overturning of ocean stratification preceded the Cambrian Explosion.

Keywords: upper Precambrian; Lower Cambrian; Iran; C-13/C-12; trace elements; paleo-oceanography

1. Geological setting and lithologic change

Strata in the Elburz Mountains of north Iran show continuous sedimentation from late Proterozoic through Cambrian time [1–3]. The fossiliferous Valiabad and Dalir sections, 60 km north of Tehran (Fig. 1), consist of two major units. The Kahar Formation (siliciclastics) of Vendian age underlies the Soltanieh Formation. The Soltanieh Formation, containing the Precambrian/Cambrian (PC/C) boundary, has five members, with carbonate and shale lithologies (Fig. 2).

Dolomite Members comprise microbial mat, tempestite, rhythmic lamination, produced by tidal currents, and gypsiferous horizons. These structures indicate a shallow water, stormy, tidal flat environment. Dolomitization was an early diagenetic process, as found in the modern sabkha environment.

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PII S0012-821X(97)00014-9

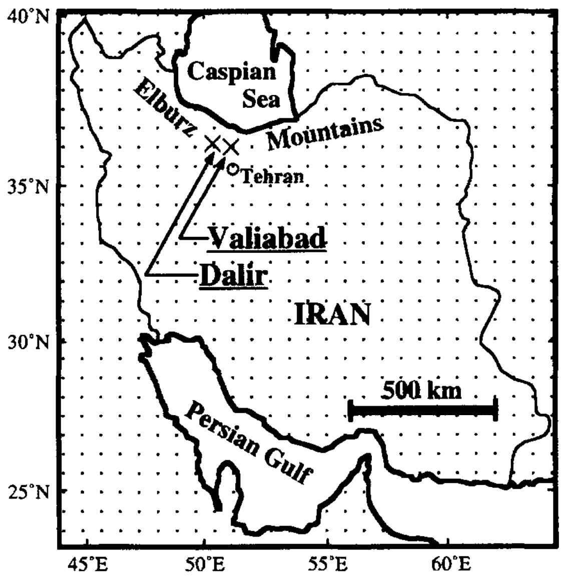


Fig. 1. Location map of the sucessions examined.

Shale members have slumps and rhythmically interbedded carbonate layers (< 1 m). Carbonate textures vary from wackestone to mudstone, and contain abundant fossil spicules. They record an open marine subtidal environment. The Lower Shale Member contains black shale and abundant fossil phytoplankton (acritarchs), such as *Chuaria circularis* and *Vendotaenia* sp. The basal part of the Upper Shale Member is a white-weathering gray shale with a high phosphate content. Also, phosphate-rich carbonate associated with iron oxides and cherts either replaced shells or formed synsedimentary collophane with normal grading.

The PC/C boundary occurs near the top of the Lower Shale Member, where early skeletal fossils such as *Protohertzina anabarica* appear, and the Upper Shale Member contains Tommotian fossils [1–3]. Small, shelly fossils that first appear in the Vendian Lower Dolomite Member increase in abundance upwards to the Middle Dolomite Member, and reach maximum abundance in the basal part of the Upper Shale Member. Both the abundance and size of trace fossils increase markedly near the boundary. They only occur, however, in the shale, so that their point of increase is difficult to identify.

2. Analytical methods

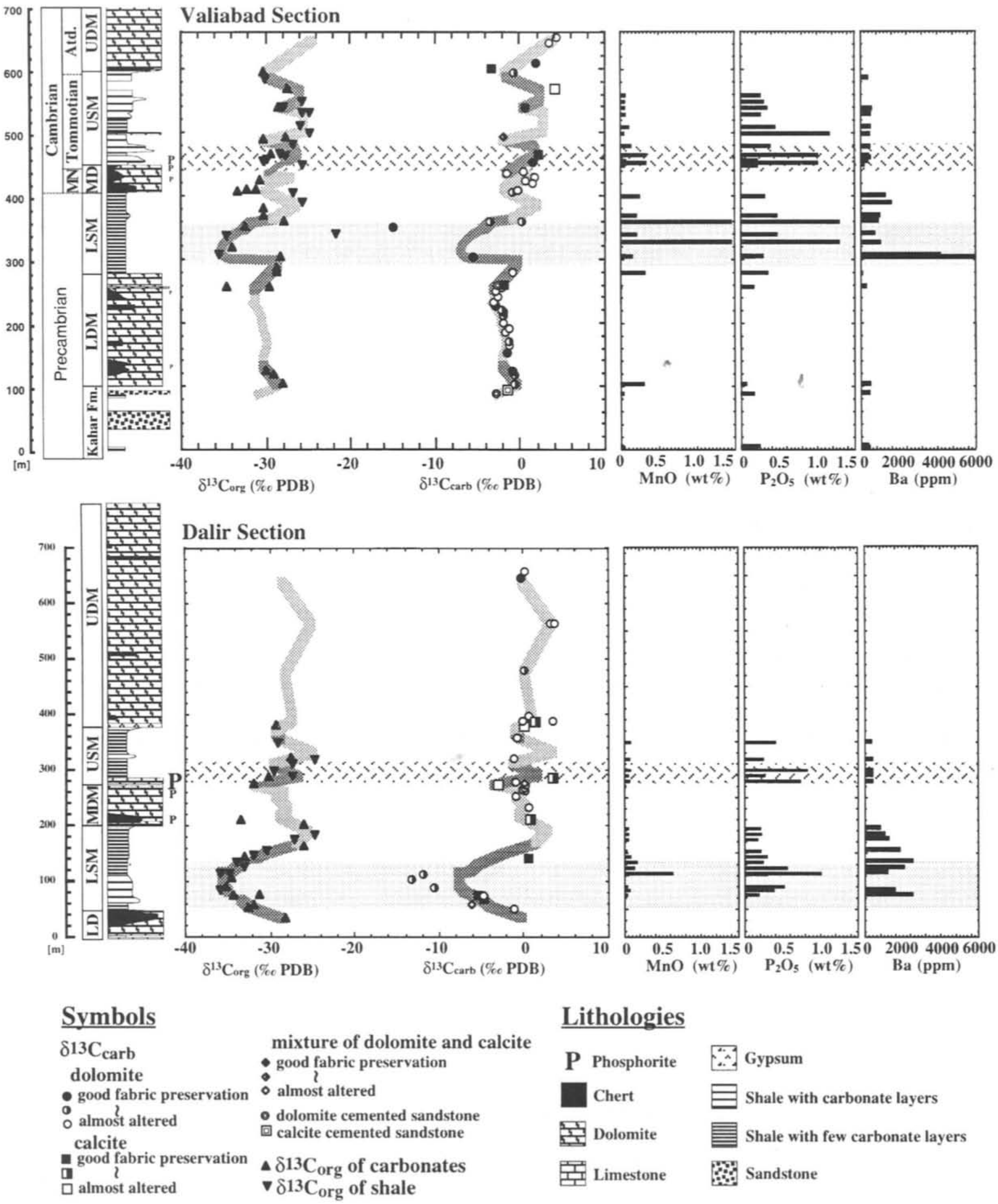
Mineralogy was determined on a Mac Science M03XHF X-ray diffractometer. The CO_2 of carbonates was liberated from whole-rock powders of carbonates using 100% phosphoric acid at 25°C. For analysis of $\delta^{13}C_{org}$, cold and then hot concentrated HCl removed carbonates from sample powders. The residue was then mixed with CuO, and combusted in sealed quartz tubes at 800°C for 3 h. $\delta^{13}C$ was analyzed on a Finnigan Mat Delta-E mass spectrometer. The overall uncertainties of $\delta^{13}C$ values are within ± 0.1‰.

The chemical compositions of shales were measured on X-ray fluorescence analyzers (Rigaku 3270 for major elements and Philips PW1480 for trace elements). The uncertainties of Mn, P, and Ba are ± 1.4%, 1.2% and 10.3%, respectively.

3. Results of analysis

Data of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ exhibit co-variation ($\delta^{13}C_{carb} = \delta^{13}C_{org} + 28.9$, $\sigma = 2.1$) throughout both successions in Valiabad and Dalir (Fig. 2). General patterns of chemical and isotopic variations are quite similar in both sections, despite faulting in the Lower Dolomite Member at Dalir. Values of $\delta^{13}C_{carb}$ vary around -2‰, with slight fluctuations (2.5‰) in the Lower Dolomite Member. $\delta^{13}C_{carb}$ is approximately $+1$‰ with high fluctuations (4‰) from the upper Lower Shale Member to the lower Upper Dolomite Member. A remarkable negative

Fig. 2. Stratigraphic columns, variations in $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and concentrations of Mn, P_2O_5, and Ba in the shale across the Precambrian/Cambrian boundary at the Valiabad section, and Dalir section, in the Elburz Mountains, Iran. The Soltanieh Formation is subdivided into the Lower Dolomite Member (*LD* or *LDM*), the Lower Shale Member (*LSM*), the Middle Dolomite Member (*MD* or *MDM*), the Upper Shale Member (*USM*) and the Upper Dolomite Member (*UDM*). *MN* = Manykayan Stage; *Atd* = Atdabanian Stage. Curves of $\delta^{13}C$ were drawn using values from both carbonate and organic phases (dark curves), or values of either the former or the latter (light curves) ($\delta^{13}C_{carb} - \delta^{13}C_{org} = 28.9$‰).


Valiabad Section
Cambrian
Precambrian
Atd.
Tommotian
MN
UDM
USM
MD
LSM
LDM
Kahar Fm.
[m]
δ13Corg (‰ PDB)
δ13Ccarb (‰ PDB)
MnO (wt%)
P2O5 (wt%)
Ba (ppm)
Dalir Section
UDM
USM
MDM
LSM
LD
Symbols
δ13Ccarb
dolomite
good fabric preservation
almost altered
calcite
good fabric preservation
almost altered
mixture of dolomite and calcite
good fabric preservation
almost altered
dolomite cemented sandstone
calcite cemented sandstone
δ13Corg of carbonates
δ13Corg of shale
Lithologies
P Phosphorite
Chert
Dolomite
Limestone
Gypsum
Shale with carbonate layers
Shale with few carbonate layers
Sandstone

excursion of $\delta^{13}C$ (-7 or $-9‰$) occurs in both carbonate and organic phases in the middle part of the Lower Shale Member. Anomalous high concentrations of MnO (~ 1.5%), P_2O_5 (~ 1.3%) and Ba (~ 6000 ppm) in shales occur with the strong negative excursion. The moderate positive excursion of $\delta^{13}C$ in the basal part of the Upper Shale Member (basal Tommotian) coincides with maximum values of 0.4% MnO and 1.0% P_2O_5.

In summary, both chemical and isotopic anomalies are stratigraphically congruent with the lithology and fossil occurrence. The strong negative excursion of $\delta^{13}C$ with high concentrations of Mn, P, and Ba occurs in black shale with abundant acritarchs. The moderate positive excursion of $\delta^{13}C$ and high concentration of phosphorus in the Tommotian stage culminates with the occurrence of phosphorites and small shelly fossils.

4. Discussion

4.1. Does the $\delta^{13}C$ profile represent an original marine signature?

The parallel fluctuation of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ strongly suggests that the negative excursion is a primary isotopic signature of seawater. No other mechanism could cause such a co-variation. Most $\delta^{13}C_{carb}$ values lie on the general trend regardless of mineralogy, original fabric preservation and localities (Fig. 2). Thus, diagenetic components are negligible.

4.2. Is the negative $\delta^{13}C$ excursion below the PC/C boundary a global phenomenon?

Previous works have shown much interest in the worldwide positive excursions of $\delta^{13}C$ in the lowermost Cambrian strata (e.g., [2,4–7,9–11]), but only a few workers have paid attention to the negative excursions (e.g., [4,5,8,9,11–16]). Ripperdan [11] considered that a single negative excursion occurs in the Neoproterozoic successions (except for the lower Cambrian example of the Yangtze Gorge [13]), but other workers (e.g., [17,18]) have recognized multiple negative excursions, which are divided into basal Vendian [12,14], uppermost Vendian [4,5,8,9,15,16,18], and early Cambrian [11,13] events. The uppermost Vendian negative excursion considered here has recently become a subject for discussion (e.g., [18]).

Detailed and precise correlation of the upper Vendian based on biostratigraphy is still impossible because of the lack of fossil key markers. Carbon isotope event stratigraphy may help us to correlate the negative excursion, if we assume that no major lacunas exist. We have used the two positive excursion events in the earliest Cambrian from chronostratigraphically well constrained profiles (Morocco [4], Siberia [9], Oman [15], and Northwest Canada [16]) for this correlation. Assuming a constant sedimentation rate for each succession, the negative excursion event occurs at nearly the same horizon (Fig. 3). The five correlated successions have different lithologies and were on different continental plates facing different oceans at that time. These may suggest that the negative excursion is a global event. The repeated association of the negative and the following positive excursions with rough fossil evidence (e.g., [5,18]) may also support the view of a global event.

4.3. A new scenario for the Cambrian Explosion

We propose that the negative $\delta^{13}C$ excursion, high concentrations of P, Mn, and Ba, abundant phytoplankton fossils, and the black shale below the PC/C boundary have all resulted from mixing of surface water and deep water.

The Earth experienced a greenhouse phase following the last Precambrian glaciation (625–550 Ma) [19–21]. During this time the latitudinal thermal gradient was small and oceanic circulation was not as vigorous as the present day. Evaporation in marginal seas at low latitudes produced warm and high salinity dense water that led to salinity stratification [21] in the world ocean. Organic matter produced by photosynthesis in the surface photic zone was bacterially degraded during passage to the sea floor. The transportation of organic matter from the surface to deep water (the biological pump) resulted in a build-up of a huge sink of total dissolved carbon (TDC) and nutrient-related elements, including phosphorus and barium. TDC in deep water was strongly depleted in ^{13}C. The consumption of free oxygen in

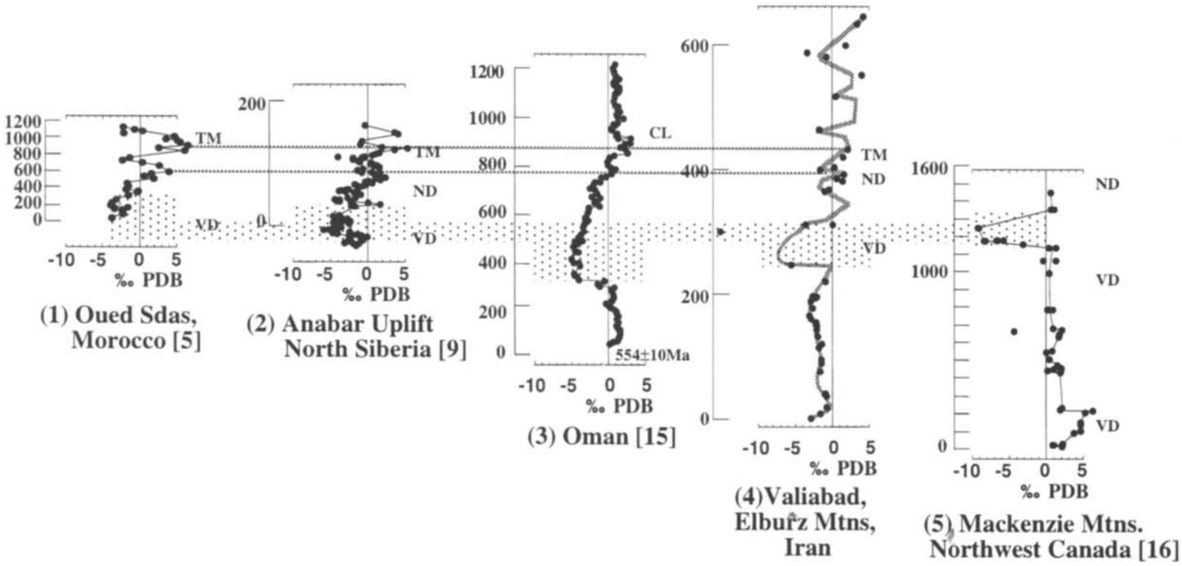


Fig. 3. Comparison of $\delta^{13}C_{carb}$ profiles across the PC/C boundary. Morocco [5], Siberia [9], Oman [15], Iran (our study) and Northwest Canada [16] are correlated here. The Anabar Uplift profile [9] is used as a representative of Siberian Platform because it is the most continuous among the Siberian profiles, all of which show very similar patterns [9]. The thickness (in meters) of strata and biostratigraphic markers are represented on the left and right sides, respectively. Correlations of $\delta^{13}C$ excursions are represented by the dotted lines. The correlation of two positive excursions is taken from previous authors [2,5,9]. *VD* = Vendian; *CL* = *Cloudina* (Vendian or possibly lowermost Cambrian [15]); *ND* = Nemakit–Daldynian; *TM* = Tommotian.

the deep water through degradation of organic matter accelerated formation of anoxic or dysoxic bottom water masses. Manganese is highly soluble in the form of Mn^{2+} under dysoxic conditions so that anoxic–dysoxic bottom waters were increasingly enriched in dissolved manganese. Thus nutrient-enriched, dysoxic, deep water masses developed below oxic surface water. The chemical and isotopic signatures of these two water masses followed totally different trends.

A typical example of stagnant oceanic condition is the present-day Black Sea. The Mediterranean Sea supplies high salinity water through the Bosphorus Strait to deep water of the Black Sea. The Mediterranean is almost a closed basin isolated from open ocean circulation. Run-off by rivers supply low salinity, surface waters to the Black Sea. The elemental (TDC, P and Ba) [22–24] and ^{13}C abundances [25] are different in surface and deep water (Fig. 4). They increase gradually with depth in the deep water mass where sluggish circulation occurs. Mn abundance reflects the different redox conditions in the oxic surface water and the permanently anoxic deep water [22] (Fig. 4).

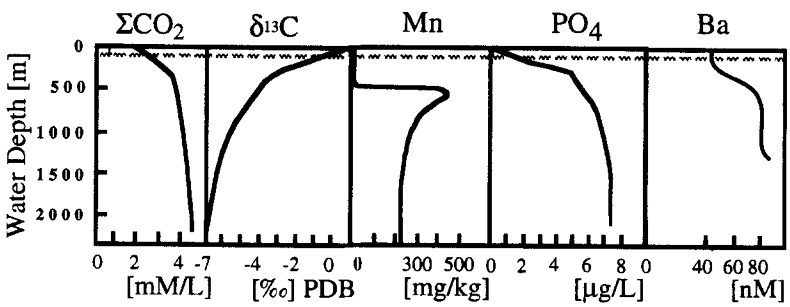


Fig. 4. Black Sea depth profiles of selected elements, taken from [22–25]. The dotted line shows the surface–deep water boundary.

Overturn of the stratified ocean caused dramatic changes in ocean environments: (1) shallow water carbonate and organic matter became strongly depleted in ^{13}C, reflecting mixing with deep water CO_2 having extremely negative $\delta^{13}C$ values; (2) manganese and barium from anoxic deep water precipitated as oxide and sulfate, respectively, in the oxic surface environment, and accumulated in shallow water sediments; and (3) phytoplankton in the photic zone flourished because of upwelled, nutrient-enriched, deep water, and was deposited as black and fossiliferous sediments.

The scenario of the oceanic overturn well explains the coincidence of negative $\delta^{13}C$ excursions, the occurrence of positive trace element anomalies, the deposition of black shale and abundant phytoplankton fossils. Alternate models for the origin of the negative $\delta^{13}C$ excursions include: decreased total biomass [26]; Strangelove ocean [13,27]; respiring ocean [27]; and a massive influx of volcanic-derived CO_2 [28]. All of these provide no explanation for the anomalously high concentration of Mn, P and Ba. Explosive diversification in the earliest Cambrian occurs stratigraphically just above the negative excursion of $\delta^{13}C$. We conclude that the Cambrian Faunal Explosion followed the latest Proterozoic overturning of oceanic stratification.

A similar oceanographic model explains the latest Permian negative $\delta^{13}C$ excursion associated with the faunal mass extinction event [29,30]. Cambrian-type small shelly fossils occur stratigraphically beneath the negative $\delta^{13}C$ excursion [1–3], but the sporadic occurrences of the Ediacaran fauna [16,17] do not clearly confirm stratigraphic association of its extinction and the negative excursion. This may imply that Phanerozoic type metazoa occupied the Ediacaran niche around the negative carbon isotope event, as during other Phanerozoic extinction events.

Acknowledgements

This is a report of the joint project between the University of Tokyo and the Geological Survey of Iran. We thank A. Hushmandzadeh (Geological Survey of Iran) for organizing the 1993 field trip, and M. Almasian (Treatise on the Geology of Iran), Y. Lasemi (Teacher's University of Tehran), Jiang Zhiwen (Yunnan Institute of Geological Sciences) for collaboration with us during field work. HK thanks T. Irino, H. Hagiya (University of Tokyo) for sharing laboratory techniques, and T. Ishii (University of Tokyo) for giving laboratory facilities. We thank J.R. Hein (US Geological Survey), P.E. Schenk (Dalhousie University), A.H. Knoll (Harvard University), Y. Kolodny (Hebrew University), S.M. Stanley (Johns Hopkins University), and Y. Watanabe (Geological Survey of Japan) for helpful comments which improved the manuscript. Grants-in-Aid from the Ministry of Education of Japan (No. 073882 to HK and No. 07041094 to RM), and JSPS Research Fellowship to HK partly funded this project. *[MK]*

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