## Sedimentary Provenance Analysis of the Ordovician Ponón Trehué Formation, San Rafael Block, Mendoza-Argentina

# Paulina Abre, Carlos A. Cingolani, Norberto Javier Uriz and Aron Siccardi

Abstract The present chapter deals with provenance analysis of a carbonate-siliciclastic Ordovician sedimentary unit of the San Rafael block, named the Ponón Trehué Formation (Darriwilian to Sandbian). This is the only sequence which exhibits a direct contact with the Mesoproterozoic basement through an unconformity, not only within the San Rafael block, but rather for the entire Cuyania terrane. When combining different provenance proxies, such as petrography, whole-rock geochemistry, Sm-Nd data, Pb-Pb analyses, and detrital zircon dating, it can be deduced that the source rocks are characterized by: (i) an upper continental crust composition, (ii) a subordinated influence of a more depleted composition, (iii) a dominantly Mesoproterozoic age, (iv) sedimentary recycling did not conspicuously affected the detrital source, and (v) weathering was relatively strong. All these characteristics point to the Mesoproterozoic Cerro La Ventana Formation basement as a main source of detritus to a restricted basin infilled during the Ordovician.

**Keywords** Geochemistry • Isotope geochemistry • Detrital zircon dating • Provenance • Ponón Trehué Formation • Cuyania terrane

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#### 1 Introduction

The Darriwilian to Sandbian Ponón Trehué Formation crops out at the southern edge of the San Rafael Block (Cuyania terrane), Mendoza province, Argentina (Fig. 1a, b). It is an olistostromic carbonate–siliciclastic sequence unconformably overlying (Fig. 2a, b), the Mesoproterozoic basement known as the Cerro La Ventana Formation (Nuñez 1979; Criado Roqué and Ibañez 1979; Heredia 1996; Cingolani and Varela 1999; Beresi and Heredia 2003; Cingolani et al. 2005; Heredia 2006). The unit comprises outcrops of the previously known Lindero Formation (Nuñez 1979 and see discussion in Heredia 1996, 2006 and Abre et al. 2011).

The continental Carboniferous Pájaro Bobo Formation (correlated with El Imperial Formation towards the Northwest of San Rafael Block) overlies the Ponón Trehué sequence through either an unconformity or a fault contact.

As an Ordovician fossil-rich unit (see Fig. 3), it contains trilobites, brachiopods, ostracods, fragmentary crinoids, corals and conodonts (Nuñez 1962; Baldis and Blasco 1973; Rossi de García et al. 1974; Levy and Nullo 1975; Heredia 2006). The



**Fig. 1** a Geological sketch map of the pre-Carboniferous units within the San Rafael block (from González Díaz 1982). Outcrops of the Ponón Trehué Formation are located southwards and unconformably overlying the Cerro La Ventana basement. **b** Detailed geology of the Ponón Trehué area, with outcrops of the Ponón Trehué Formation in the central part (areas named 1, 2 and 3). Modified from Nuñez (1979), Cingolani and Varela (1999), and Cingolani et al. (2005)



**Fig. 2** a General view towards the North of the Ordovician Ponón Trehué limestones in contact with the Mesoproterozoic basement. **b** Outcrops of the Ponón Trehué fossiliferous limestones near the homonymous creek showing the remnants of the carbonate platform that slumped down the slope margin

first fossiliferous record was made by Nuñez (1962). This material was preliminary classified by Armando F. Leanza as the brachiopods *Obolus* and *Taffia*, and the trilobite *Lonchodomas* cf *salagastensis* (Rusconi). These records have been used to



**Fig. 3** Ordovician fossils known in the Ponón Trehué Formation (after Nuñez 1962; Baldis and Blasco 1973; Levy and Nullo 1975). BRACHIOPODS: *Ptychoglyptus mendocina Levy and Nullo*, *1075*: (1) ventral valve; (2) dorsal valve; (3) valve showing costulation. *Nugnecella rafaelensis Levy and Nullo*, 1975: (4) ventral valve; (5–6) dorsal valve; (7) ventral valve. TRILOBITES: "*Elbaspis*" (*Miraspis?*) *pintadensis* Baldis and Blasco, 1973: (8a) dorsal view of cranidium, (8b) reconstruction of the cranidium; (9) "*Flexycalymene*" (*Reacalymene*) *frontalis* Baldis and Blasco, 1973: (*10a–b*) dorsal view of cranidium (*10c*) reconstruction of the cranidium in dorsal view; *Ampyx nunezi* Baldis and Blasco, 1973: (*11a*) pygidium, internal mold, (*11b*) reconstruction of the pygidium, (*11c*) cranidium in dorsal view; (*11d*) reconstruction of Asociación Paleontológica Argentina, Buenos Aires

correlate the Ponón Trehué unit with the Middle Ordovician San Juan Limestones, cropping out in the Precordillera region, as was first mentioned by Wichmann (1928) that considered the carbonates similar to those of Cerro de la Cal and Salagasta (near the city of Mendoza). Baldis and Blasco (1973) revised in detail the trilobite material and described the new genus *Elbaspis (Odontopleuridae*,

Selenopeltinae) (? = Miraspis; Ramsköld 1991; Jell and Adrain 2003) and the new species Elbaspis pintadensis, Toernquistia chinchensis (Dimeropygidae) (reassigned to Paratoernquistia by Chatterton et al. 1998), Ampyx nunezi (Raphiophoridae), and Flexicalymene frontalis (Calymenidae). Undeterminable species of Monorakidae, Trinucleidae, and Illaeninae are also present in the assemblage (see Fig. 3).

At the northern sector (in the way to the Chinches Hill) in small outcrops of Ponón Trehué Formation, some stromatolite structures were recognized in limestone rocks preserved as olistoliths.

The Ponón Trehué Formation is subdivided into two members: the lowermost (Peletay Member) is composed of conglomerates and conglomeratic arkoses, limestones, quartz arenites, and black shales, whereas the uppermost (Los Leones Member) is composed of mudstones, siltstones, arenites, and conglomeratic arenites.

The extension undergone by the Cuyania terrane after its accretion to Gondwana produced the brecciation of parts of the carbonate platform (Fig. 2a, b) that slumped down the slope, forming this breccia-type deposit (Astini 2002) within a fine clastic matrix. The absence of blocks from the Cambrian carbonate platform indicates that for the time of deposition of the Ponón Trehué Formation the basement was exposed (Heredia 2006).

Determining the paleogeographic and paleoclimatic conditions of deposition within a certain basin may be achieved by means of sedimentary provenance analysis, since sedimentary siliciclastic rocks record characteristics of their source rocks and areas. The final composition of a sedimentary rock does not depend solely on the original composition of the parent rock due to the effects that other processes such as weathering, sorting during transport, sedimentary recycling, and diagenesis would imprint. Therefore, several provenance techniques should be applied together, if possible, since each dataset would reveal different aspects of the parent material and/or the changes in composition that the sediments have suffered through their history. The provenance of the Ponón Trehué Formation was determined using petrography, whole-rock geochemistry and isotope geochemistry (including detrital zircon dating).

#### 2 Petrography

The Ponón Trehué Formation at the La Tortuga section (35° 10′ 53″S–68° 18′ 13″W) comprises claystones, siltstones and fine-grained sublith- and subfeldspathic arenites (Dott 1964). The arenites are moderately sorted with scarce matrix. The framework minerals include: subrounded to subangular monocrystalline (with low sphericity) and polycrystalline (less abundant) quartz as well as subrounded K-feldspar commonly totally replaced by chlorite or clay minerals; detrital muscovite lamellae are very scarce. Sedimentary lithoclasts derived from siltstones, carbonates, mudstones, and cherts were also described. When present, the cement is composed

Air-dried samples			
Sample	FWHM	CIS	Diagenesis/Metamorphisms
CT3	0.328	0.378	Low anchizone
CT6	0.318	0.370	Low anchizone
CT7	0.274	0.339	Low anchizone
CT8	0.334	0.382	Low anchizone
Ethylene-glycol attacked samples			
CT3	0.322	0.373	Low anchizone
CT6	0.313	0.367	Low anchizone
CT7	0.275	0.339	Low anchizone
CT8	0.329	0.379	Low anchizone

 Table 1
 Illite crystallinity index measured to determine the grade of diagenesis and/or very low-grade metamorphism of the Ponón Trehué Formation

FWHM full-width-height-maximum. CIS crystallization index corrected according to standardized values. For details on methodology see Abre (2007). The term anchizone is equivalent to very low-grade metamorphism according to the recommendations of the Subcommission on the Systematics of Metamorphic Rocks from the IUGS (Árkai et al. 2003)

of calcite. The heavy minerals fraction comprises zircon, apatite, chromian spinel, tourmaline, rutile, and iron oxides such as hematite. X-ray diffraction analyses indicate that clay minerals within the three lithotypes are mainly chlorite, sericite, and illite (Abre 2007; Abre et al. 2011).

Sandstones of the Ponón Trehué Formation had shown relatively textural immaturity and mineralogical maturity, which altogether may imply that the detritus had suffered low transport but a certain degree of chemical weathering. The composition of the lithoclasts indicates sedimentary rocks as part of the source, while the presence of detrital chromian spinels clearly points to a mafic source. The bulk of the mineralogical composition indicates felsic sources.

The 'illite crystallinity index' (ICI; Kübler 1966 in Warr and Rice 1994) is defined as the width of the (001) XRD peak at half of its height, and it is used to determine either the grade of diagenesis or the very low-grade metamorphism that a clastic rock could have suffered. A well-crystallized illite, characteristic of a relatively high-temperature history, has sharp peaks, and therefore a low index, while low-temperature illite is more disordered, and has irregular peaks with large indexes. The ICI on four fine-grained clastic samples of the Ponón Trehué Formation shows that the unit was affected by very low-grade metamorphism (Table 1).

#### **3** Whole-Rock Geochemistry

Geochemical analyses quantify bulk composition of a rock and give additional information to petrographic data regarding provenance and processes that might have modified the original composition. Major elements have been proved useful for weathering analysis, whereas certain trace elements (particularly REE) and their ratios are used to characterize the composition of the source (or the mix of sources) and would indicate tectonic setting. Furthermore, elements easily affected during weathering and diagenesis would permit to evaluate to which extent the bulk chemical composition of the detrital rock would have been affected by these processes.

**Weathering**: The degree of primary material transformation due to weathering can be estimated using the Chemical Index of Alteration (CIA; Nesbitt and Young 1982):

$$CIA = \{Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)\} \times 100,$$

where CaO<sup>\*</sup> refers to the calcium associated with silicate minerals and the index is calculated using mole fractions. Index values vary between around 50 for unweathered crystalline rocks to 100 for kaolinitic residues. CIA values of the Ponón Trehué Formation (n = 8) ranges from 69 to 77 and samples are grouped toward the A-K boundary and close to the muscovite idealized composition, in accordance to XRD mineralogical data (Fig. 4a). Their distribution on the A-CN-K space does not correspond to a normal weathering path; furthermore, only two samples show a slight  $K_2O$  enrichment comparing to upper continental crust (UCC) values. Therefore, the very low-grade metamorphism indicated by ICI should explain the behavior of samples from the Ponón Trehué Formation, although effects of source mixing cannot be ruled out. Since the CIA values seem to have been modified, they can be recalculated using the expected weathering path of the average UCC, assuming such a composition for the source rocks (Fedo et al. 1995; Bock et al. 1998). In Fig. 3a, the dashed lines go from the K apex through the samples with the lowest and highest CIA and toward the normal weathering path for the UCC. Dotted lines end on the CIA scale indicating the corresponding CIA recalculated value for that interval, which would now range from 76 to 81, indicating strong weathering (Fedo et al. 1995), as it was deduced by petrographic analysis (Abre 2007; Abre et al. 2011).

The Th/U ratios have been used to estimate weathering effects in sedimentary rocks (McLennan et al. 1993), however, for the Ponón Trehué Formation results are not conclusive since some samples show Th/U ratios typical for unrecycled sediments (around 3.5–4; McLennan 1989), while others show U enrichment (therefore not indicative of weathering) and others do show values suggesting weathering (Abre et al. 2011).

**Recycling**: During reworking there is a tendency to increase stable heavy minerals content, particularly zircon (main Zr carrier), and therefore certain ratios such as the Zr/Sc would also increase (McLennan et al. 1993). The spread of Zr/Sc ratios of the Ponón Trehué Formation shows a cluster of data indicating that processes of recycling were not important, which is in accordance to petrographic characteristics such as relatively textural immaturity.

Source composition: Certain trace elements and their ratios are useful for provenance determination due to their preference either for felsic (Zr, Y, Th) or



Fig. 4 Whole rock geochemical data obtained from Abre (2007) and Abre et al. (2011). a A-CN-K diagram; UCC, PAAS and idealized mineral compositions are according to Taylor and McLennan (1985). Field of vertical lines indicates the predicted weathering trend for the average UCC. Note that the *lower part* of the diagram with A < 40 is not shown. The *left side of the figure* shows the range of CIA values corrected according to Fedo et al. (1995). b La/Th versus Hf for samples of the Ponón Trehué Formation. La/Th ratios of 2-4 are common values for upper crust composition and indicate felsic compositions (McLennan et al. 1980). c The input of a mafic source could be discriminated using the Y/Ni and Cr/V ratios (McLennan et al. 1993). The Y/Ni ratio indicates the concentration of ferromagnesian trace elements (e.g. Ni) compared with a proxy for HREE (represented by Y). The Cr/V ratio indicates the enrichment of Cr over other ferromagnesian trace elements. Ophiolitic components would have Cr/V ratios higher than 10 (discussion in McLennan et al. 1993). UCC values according to McLennan et al. (2006), while PAAS is following Taylor and McLennan (1985). d Upper continental crust-normalized multielement patterns; elements are arranged from left to right in order of decreasing ocean residence time and comprise a relatively mobile group (from K to Ni) and a more stable group (from Ta to Th). Normalization values are from Taylor and McLennan (1985), except for P and Yb which are from McLennan et al. (2006). For a, b and c sandstones are represented by circles while mudstones are by squares

mafic (Sc, Cr, V) facies during melt crystallization (Taylor and McLennan 1985). Rare earth elements (REE) patterns in well-mixed sedimentary rocks also represent reliable provenance indicators (McLennan 1989). The Th/Sc ratios indicate that the source of detritus for the Ponón Trehué unit had dominantly a typical upper continental crustal composition (Abre et al. 2011). La/Th ratios between 2.58 and 4.05 (Fig. 4b) further support such a felsic dominant composition for the source rocks. However, contents of Sc (up to 20 ppm), Cr (up to 240 ppm) and V (up to 193 ppm), and Cr/V ratios higher than the UCC values, and Y/Ni ratios lower than

the UCC indicate the influence of a source with a composition less evolved than the average UCC, although an ophiolitic source can be neglected (Fig. 4c). The mafic input is also documented by chromian spinels (Abre et al. 2011).

The chondrite normalized REE patterns for the Ponón Trehué Formation show certain enrichment of LREE ( $La_N/Yb_N$  of about 5.8 on average), as well as HREE ( $Tb_N/Yb_N$  of 1.17 on average) compared with the Post-Archaean Australian Shales (PAAS). The negative Eu-anomaly ( $Eu_N/Eu^*$  of about 0.52 on average) typical for detrital rocks derived from UCC is present.

**Tectonic setting:** Using Bhatia and Crook (1986) tectonic classification diagrams, a continental arc or an active continental margin was deduced for the Ponón Trehué Formation (Abre et al. 2011). Since the continental arc setting represent convergent plate margins and the active continental margin setting comprises the Andean-type and strike-slip continental margins (Bhatia and Crook 1986), such provenance proxie was not enough to determine the tectonic setting of the basin to aid on palaeogeographic reconstructions.

Upper continental crust-normalized multielement patterns have proven useful to describe the range of compositions of greywackes as a result of the tectonic environment (Floyd et al. 1991). The Ponón Trehué Formation shows (Fig. 4d): (1) negative Sr anomalies typical of passive margin settings, (2) positive V–Cr–Ni–Ti–Sc anomalies indicative of mafic inputs, (3) Nb similar to UCC with exception of samples CT1 and CT2, (4) positive Hf–Zr–Y anomalies that can be related to heavy mineral contents (particularly zircon) which typically increases in passive margin settings; noteworthy are the negative anomalies for samples CT1 and CT2, (5) the most stable element ratios are close to 1, feature generally indicative of a continental arc/active margin tectonic environment.

In conclusion, the multielement patterns confirm that the source comprised a mafic component typical of active margins, although anomalies related to passive margins are present. The behavior of samples CT1 and CT2 is clearly related to high silica contents (more than 79 %) linked to intense weathering in a continental active margin rather than in an oceanic setting.

#### 4 Isotope Geochemistry

**Sm–Nd**: The Sm–Nd isotope system is a good provenance indicator since it aids to determine the grade of fractionation and the average crustal residence time of the detrital mix (McLennan et al. 1990), because the system is usually not resetted by erosion, sedimentation, and high-grade metamorphism (DePaolo 1981). According to Abre et al. (2011) the  $\varepsilon_{Nd}(t)$  values, where t = 462 Ma (depositional age) ranges from -3.95 to -4.91 for the Ponón Trehué Formation (average  $-4.47 \pm 0.39$ ).  $f_{Sm/Nd}$  ranges from -0.34 to -0.40 (average  $-0.37 \pm 0.02$ ), while  $T_{DM}$  ages ranges from 1.3 to 1.52 Ga (average  $1.44 \pm 0.078$  Ga). These values are neither typical of an old upper crust nor of an arc component.  $\varepsilon_{Nd}(t)$  values are similar to those from other Ordovician sedimentary rocks from the Cuyania terrane (Abre 2007; Gleason



**Fig. 5**  $\varepsilon_{Nd}$  versus age of the Ponón Trehué Formation. The range of the Mesoproterozoic Cerro La Ventana Formation Nd data is drawn for comparison (Cingolani et al. 2005). *CHUR* Chondritic Uniform Reservoir

et al. 2007; Abre et al., this volume), as well as from rocks of the Famatinian arc (Pankhurst et al. 1998) and are in the range of variation of data from the Cerro La Ventana Formation (Fig. 5) calculated to the time of deposition of the Ponón Trehué Formation.

**Pb–Pb**: <sup>206</sup>Pb/<sup>204</sup>Pb ranges from 19.028 to 19.303 and <sup>208</sup>Pb/<sup>204</sup>Pb ranges from 38.83 to 38.99 (Abre et al. 2011). The radiogenic lead (<sup>207</sup>Pb/<sup>204</sup>Pb) is interesting since most terrestrial <sup>207</sup>Pb was produced early in the Earth's history and therefore the high <sup>207</sup>Pb/<sup>204</sup>Pb ratio of these samples (15.66–15.71) might suggest the input from an old Pb component to the sedimentary succession (Hemming and McLennan 2001). Analyzing both, uranogenic- and thorogenic-Pb it is evident that samples from the Ponón Trehué Formation plot slightly above the Stacey and Kramers (1975) second stage Pb evolution curve for average crust and they are more similar to those from the globally subducted sediment (GLOSS) average than the upper continental crust composition (Fig. 6) being more comparable with samples from trailing edges and continental collision zones (Hemming and McLennan 2001). The Pb system of the Ponón Trehué Formation differs consistently from the Mesoproterozoic Cerro La Ventana Formation (Fig. 6), although it is not possible to know whether this is due to isotopes remobilization during weathering and low-grade metamorphism or if it would point to a different source.

**U–Pb detrital zircon**: Age determination of individual detrital zircon grains has been proved a powerful tool for provenance discrimination, particularly when determining age of intermediate to felsic source rocks. Detrital zircon dates (n = 38) of the Ponón Trehué Formation cluster between 1065 and 1277 Ma with a main



**Fig. 6** a  ${}^{207}\text{Pb}/{}^{204}\text{Pb}$  versus  ${}^{206}\text{Pb}/{}^{204}\text{Pb}$  and b  ${}^{208}\text{Pb}/{}^{204}\text{Pb}$  versus  ${}^{206}\text{Pb}/{}^{204}\text{Pb}$  present-day ratios. *Brown areas* represent samples from the Ponón Trehué Formation; *solid square* is the average value for the upper crust and *solid circle* the average value for GLOSS, both from Hemming and McLennan (2001). *SK* Stacey and Kramers reference line. Samples from the Cerro La Ventana Formation are shown for comparison (data from Cingolani et al., this volume)

peak at about 1200 Ma (Fig. 7). Only one discordant grain has a younger age of 834 Ma (Abre et al. 2011). The very narrow range of detrital zircon ages implies a local and restricted provenance, most likely from the underlying Cerro La Ventana Formation and is in agreement with the low recycling deduced from petrographic and geochemical analyses. Th/U ratios measured in zircons along with cathodo-luminescence images indicate a dominance of grains originated by magmatic processes rather than metamorphic. The Cerro La Ventana Formation, with ages between 1.1 and 1.2 Ga (Cingolani and Varela 1999; Cingolani et al. 2005), matches the detrital zircon ages and was a source of detritus. Other



**Fig. 7** U–Pb distribution of analyzed detrital zircons with probability curves for the Ponón Trehué Formation. Representative cathodoluminescense microphotographs of selected zircon grains used for detrital dating show the predominance of magmatic internal textures. Bar length is 100 µm and ages are in Ma (Abre et al. 2011)

Mesoproterozoic rocks within the basement of the Cuyania terrane are found at the Pie de Palo Range (1.0–1.2 Ga; McDonough et al. 1993) and the Umango, Maz and Espinal Ranges (1.0–1.2 Ga; Varela and Dalla Salda 1992; Varela et al. 1996; Casquet et al. 2006; Rapela et al. 2010; Varela et al. 2011).

#### 5 Discussion

The petrographic analyses of the Ordovician Ponón Trehué Formation showed the dominance of monocrystalline quartz and K-feldspar and the presence of sedimentary lithoclasts (siltstones, carbonates, mudstones and chert) and spinels, which point to an upper continental crustal component (including the recycling of sedimentary rocks) and the influence of a source less evolved than the UCC. Geochemical analyses of the Ponón Trehué Formation indicate strong weathering and other secondary processes, since high CIA values are present and potassium enrichments were detected. The dominance of an upper continental crustal component is clearly reflected, but relatively high abundances of compatible elements along with low Th/Sc ratios suggest a mafic input, although an ophiolitic source can be neglected based on Y/Ni and Cr/V ratios. Recycling was not important, according to low Zr/Sc ratios, pointing to source rocks closely related to the depositional basin.

Sm–Nd isotopes indicate a narrow range of variation with  $\varepsilon_{Nd}$  value of about –4.5, a  $f_{Sm/Nd}$  of about –0.37 and  $T_{DM}$  of 1.44 Ga. Pb isotopes for the Ponón Trehué Formation indicate that at least a part of the components has a "Gondwanan Pb-signature," characterized by high <sup>207</sup>Pb/<sup>204</sup>Pb ratios. Zircon dating constrains the age of the main sources to the Mesoproterozoic, with a main peak at 1.2 Ga.

Sedimentological characteristics indicate a dominant provenance from the underlying Mesoproterozoic Cerro La Ventana Formation (Heredia 2006). The basement consists of mafic to intermediate gneisses, foliated quartz diorites, and tonalites that partially graded to amphibolites and migmatites, as well as acidic to intermediate granitoids and pegmatitic and aplitic veins (Cingolani et al. 2005; Cingolani et al., this volume). Nd data presented by Cingolani et al. (2005) of the Cerro La Ventana Formation show  $\varepsilon_{Nd}$  values in the range of variation of data calculated to the time of deposition of the Ponón Trehué Formation. Sm–Nd, Rb–Sr, and U–Pb on zircons indicate Mesoproterozoic ages (1.1–1.2 Ga; Cingolani et al. 2012), which fit detrital zircon data from the Ponón Trehué Formation.

The Ponón Trehué Formation is an olistostromic sequence deposited within a restricted basin and the sediment supply was from a local source (the Cerro La Ventana Formation). Considering that the Cerro La Ventana Formation is the most probable source area, it would have been uplifted since at least the Darriwilian in order to provide detritus to the Ponón Trehué basin.

#### 6 Conclusions

Petrographical and geochemical analyses of the Ponón Trehué Formation indicate a main provenance component with an upper continental crust composition but with a subordinate input from a less evolved source. The unit is strongly weathered. Th/Sc ratios indicate no important recycling.

The Nd system is similar to that from the Mesoproterozoic basement of the San Rafael block (Cerro La Ventana Formation). Pb isotopes of the Ponón Trehué Formation clearly account for an important influence of a source with high Pb ratios, particularly <sup>207</sup>Pb/<sup>204</sup>Pb. Detrital zircon dating further constrains the ages of the sources as almost exclusively Mesoproterozoic (peak at 1.2 Ga), in coincidence with a dominant provenance from the Cerro La Ventana Formation.

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