Mineralogical and geochemical evolution of a basalt-hosted fossil soil (Late Triassic, Ischigualasto Formation, northwest Argentina): Potential for paleoenvironmental reconstruction

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ABSTRACT

Reconstruction of paleoclimatic conditions in the Ischigualasto basin, northwestern Argentina, has been constrained by field studies coupled with mineralogic, whole-rock, and fine-fraction chemical and stable isotope analysis of a Triassic (Carnian) basalt-hosted fossil soil. Field evidence, such as wedge-shaped aggregate structure and slickensides, indicates that this was likely a paleo-Vertisol. Whole-rock analysis defines down-profile trends in clay mineralogy and chemical composition that are consistent with modern soils developed upon basalt parent material. X-ray diffraction analysis indicates that the basaltic parent material is dominated by plagioclase with trace amounts of weathered 2:1 phyllosilicate. Overlying weathered horizons show a progressive loss of plagioclase and an increase in phyllosilicates with minor amounts of kandite clays and detrital quartz. X-ray diffraction analysis of the <2 µm fraction shows that the weathered layers are dominated by dioctahedral smectite (montmorillonite) and a minor fraction of kaolinite in the upper layers of the profile. There is a progressive loss of basic cations in conjunction with an increase in concentration, on a wt% basis, of conservative elements from the basalt upward through the weathering profile. The combined data indicate that this soil likely formed on a stable landscape in a cool and humid climate. In addition, the presence of quartz in the paleosol profile suggests an eolian contribution of sediment during pedogenesis.

Despite these apparent morphologic and bulk chemical trends indicative of a pedogenic origin, none of the authigenic minerals formed in isotopic equilibrium. However, based on measured oxygen and hydrogen isotope compositions, these minerals apparently formed from meteoric waters with a narrow range of δ18O and δD compositions at different temperatures. If this is correct, then amygdaloidal calcites formed at ~60–100 °C, followed by precipitation of montmorillonites at 49–57 °C during late-stage hydrothermal alteration. Finally, goethite formed at low temperatures of 6 ± 3 °C in a pedogenic environment.

This complex history of hydrothermal alteration and pedogenic overprinting brings to light the need for cautious interpretation of bulk chemical trends in paleosols as a means for paleoclimate reconstruction. Comparison of the calculated Triassic oxygen isotopic compositions of meteoric water and soil temperature with modern environments suggests that this soil formed in a seasonal, humid, and cool climate.

Keywords: paleosols, clay mineralogy, oxygen and hydrogen isotopes of pedogenic minerals, pedoclimate, mineral weathering.

INTRODUCTION

In a detailed isotopic study of modern weathering and soil profiles developed on igneous parent rock, Lawrence and Taylor (1971, 1972) found that the D/H and 18O/16O ratio of a given authigenic clay mineral or hydroxide remains constant throughout the entire soil profile, indicating that the minerals formed at or near isotopic equilibrium with soil waters. Furthermore, Savin and Epstein (1970) and Lawrence and Taylor (1971, 1972) established that the isotopic composition of authigenic phyllosilicates and hydroxides from modern soil profiles exhibit δD and δ18O values that parallel the modern meteoric water line. This supports a meteoric origin for waters involved in subaerial weathering environments and indicates that the isotopic composition of soil-formed minerals that develop on igneous parent rock are generally not compromised by inherited clay minerals or hydroxides. Therefore, the isotopic composition of hydrated minerals that form in igneous-rock-hosted soils may provide environmental information for the time of weathering, and the relationship between the isotopic composition of soil-formed minerals in igneous-hosted fossil soils and the paleo-meteoric water line hold potential for quantifying paleoclimatic conditions.

Extrusive igneous deposits are an important lithologic component of many depositional basins (e.g., Newark Basin, Siberian and Deccan Traps, East African Rift). Pedogenic minerals formed on igneous lithologies in sedimentary basins, if critically assessed, have the potential to yield significant paleoclimatic information. To date, however, no chemical and isotopic analysis of ancient soil-formed minerals developed upon igneous materials has been presented. Here, we provide the first detailed mineral, chemical, and stable isotope (δD and δ18O) study of a Triassic soil profile developed on a basalt flow from the Ischigualasto–Villa Unión basin of northwest Argentina (Fig. 1).

The results indicate that many of the original macro- and micromorphological weathering features remain intact in the Triassic-age paleosol.

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Furthermore, geochemical trends in the weathering profile are consistent with commonly observed pedogenic weathering environments (e.g., Tardy, 1971). The suite of authigenic minerals preserved in the weathering profile are not in isotopic equilibrium, contrary to what was expected based on investigations of modern soil-weathering environments. However, the isotopic data do indicate that this suite of minerals formed from the same meteoric waters during hydrothermal alteration and subsequent low-temperature pedogenic overprinting. Although the paragenetic sequence of mineral formation in basalt flows may be quite complex, this study shows that climate reconstructions may still be made from these geologically abundant lithologies.

GEOLOGIC BACKGROUND

Tectonic Setting and Stratigraphy

The study area is located along the southern edge of the Ischigualasto–Villa Unión basin in northeastern San Juan Province, Argentina, and lies within the boundaries of the Ischigualasto Provincial Park (Fig. 1). During Mesozoic time, oceanic-continental plate interactions along the southwestern margin of Pangaea produced a region of extensional deformation cratonward of the proto-Andean magmatic arc (Ramos and Kay, 1991; Lopez-Gamundi et al., 1994). Extension was focused along the northwest-trending boundary between Paleozoic accreted terranes and the Precambrian Gondwanan craton (Uliana et al., 1989). The Ischigualasto–Villa Unión basin of northwest Argentina is one of a series of continental-rift basins that developed in the region as a result of this extension (Fig. 1B) (Uliana and Biddle, 1988).

The rocks of the Ischigualasto–Villa Unión basin are exposed adjacent to the Valle Fertil and Alto faults, both of which are interpreted to be Triassic normal faults that were reactivated in the Neogene with reverse displacement (Fig. 1C) (Milana and Alcober, 1996). Rift-related deposition in the Ischigualasto–Villa Unión basin began during Early Triassic time. Rifting continued into the Cretaceous, providing accommodation space for accumulation of >4 km of nonmarine and volcanic strata (Milana and Alcober, 1994; Alcober, 1996). The Triassic system in the basin consists of the Lower Triassic Talampaya and Tarjados Formations, the Middle Triassic Chañares/Ischichua and Los Rastros Formations, and the Upper Triassic Ischigualasto and Los Colorados Formations (Fig. 2) (Stipanicic and Bonaparte, 1979). The paleosol that is the focus of this investigation is stratigraphically situated near the base of the Ischigualasto Formation (Fig. 3) (Currie et al., 2001).

In the study area, the Ischigualasto Formation consists of ~300–700 m of mudstone, sandstone, conglomerate, and basalt. The sedimentary rocks of the formation are primarily channel and overbank deposits of fluvial systems sourced in Triassic highlands southwest of the Valle Fertil paleofault, whereas the basalts were formed by flows originating from volcanic centers located at the northeast and northwest margins of the basin (Alcober, 1996).

An Upper Triassic age of the Ischigualasto Formation is based on vertebrate fossils and a radiometric age of altered ash beds from the unit. Abundant vertebrate fossils from the lower two-thirds of the formation indicate a Carnian age of deposition (Rodgers et al., 1993; Alcober, 1996), whereas 40Ar/39Ar dating of sanidine crystals from a bentonite ~80 m above the base of the formation yielded an age of 227.8 ± 0.3 Ma (Rodgers et al., 1993). In addition, to the east of the study area near Baldecitos (Fig. 1C), basalt flows correlated with the Landinian Los Rastros Formation yielded a K/Ar age of 229 ± 5 Ma (Fig. 2) (Valencio et al., 1975; Odin et al., 1982). Collectively, these ages support a Carnian age of deposition for the lower part of the Ischigualasto Formation (Fig. 2).

The thickness of overlying units north of the study area indicates that ~2 km of additional Jurassic-Tertiary strata were deposited in the basin following Triassic deposition (Stipanicic and Bonaparte, 1979). This interpretation is supported by geochemical analysis of organic-rich shales from the Los Rastros Formation in the southern part of the basin that indicate that burial depths of the Middle Triassic stratigraphic interval did not exceed 2 km (Lopez, 1995). The rocks of the basin are presently exposed as a result of Miocene-Holocene reverse-displacement reactivation of the basin.
the Valle Fertil and Alto faults (Milana and Alcober, 1994).

**Paleoclimatic Interpretation of the Ischigualasto Basin Sedimentary Sequence**

During the Triassic, the Ischigualasto basin was situated at mid-latitudes (40°–50° S), along the southwestern edge of Gondwana (Scotese and Golonka, 1992; Smith et al., 1994). Previous workers identified a single climate cycle, from relatively dry and seasonal during the Early Triassic, to more humid during Middle Triassic deposition, then returning to seasonally dry during the Late Triassic (Stipanicic and Bonaparte, 1979; Alcober, 1996). These interpretations are based primarily on sedimentological and paleontological evidence such as the presence of red beds and braided ephemeral stream and eolian deposits in the Lower Triassic Tarjados/Talampaya Formations (Lopez-Gamunidi et al., 1989), abundant lacustrine deposits and preserved plant fossils in the Middle Triassic Chañares/Ischichuca and Los Rastros Formations, and red beds, calcareous paleosols, and evaporite deposits in the Upper Triassic Ischigualasto and Los Colorados Formations (Stipanicic and Bonaparte, 1979; Alcober, 1996). In these interpretations, the lowermost lacustrine strata of the Ischichuca Formation represent the wettest Triassic interval, while the uppermost Los Colorados Formation represents the driest interval (Alcober, 1996). The Ischigualasto Formation, therefore, represents deposition during the transition between these interpreted “wettest” and “driest” intervals.

**METHODS**

The paleosol that is the focus of this investigation is stratigraphically situated ~45 m above the base of the Ischigualasto Formation in the eastern part of the Ischigualasto Provincial Park (Figs. 1C, 3, and 4). The paleosol profile was logged and described in the field according to the methods of Retallack (1988). This unit is composed of loosely consolidated mudstones and claystones above an ~8.5-m-thick basalt flow. In order to avoid recent weathering products not associated with Triassic weathering, the outcrop face was excavated ~60 cm to provide a fresh surface for describing and sampling. Approximately 500 g of material were collected from each unit within the paleosol and stored in canvas bags. In addition, indurated Fe oxides were collected from narrow (~2 cm) ironstone bands occluding joint fractures within the basalt ~1.0 to 1.5 m beneath the surface of the paleosol. Detailed procedures and methods of mineralogical, chemical, and isotope characterization

**Figure 2.** Time-stratigraphic chart for Triassic rocks of the Ischigualasto–Villa Unión basin and relative stratigraphic position of studied paleosol and radiometrically dated horizons. Time scale adapted from Alcober (1996).

**Figure 3.** Measured section of the basal Ischigualasto Formation from the eastern region of Ischigualasto Provincial Park. Meter level corresponds to height above the base of the formation. The studied paleosol occurs at ~44–45 m (star) in the upper part of a thick basalt. See legend for explanation of lithologic symbols.
and analysis of the samples are available but are not discussed further in this manuscript.¹

RESULTS

Paleosol Morphology

A clay-rich deposit defines the upper 53 cm of an ~14-m-thick basalt flow (Fig. 3). The lower 8 m is massive, unweathered, vesicular, holocrystalline plagioclase basalt (R in Fig. 4). Some vesicles are open and others have been filled by calcite amygdules. The upper 1.0 to 1.5 m of the basalt flow exhibits areas of extensive jointing and fractures that are commonly filled with reddish-brown to black Fe oxide minerals. A 23- to 32-cm-thick zone of spheroidal alteration (Cr in Fig. 4) overlies the unweathered basalt (R). The outer "rinds" of the spheroids are clay-rich and friable, 4 to 8 cm thick, and consist of dusky red, clay-altered basalt with massive to weakly developed fine angular blocky structure (D in Figs. 4B–C). The middle rinds are 5 to 6 cm thick, greenish gray, and friable with poorly preserved calcite amygdules and waxy, green, phyllosilicate amygdules. The cores of the spheroids are light gray and range from 8 cm to 11 cm in diameter (C in Figs. 4B–C). The interiors of the spheroids are less friable and preserve calcite amygdules.

¹GSA Data Repository item 2004128, supplemental methods, is available on the Web at http://www.geosociety.org/pubs/ft2004.htm. Requests may also be sent to editing@geosociety.org.

There is a distinct (2–5 cm thick) transition from the spheroidal zone to a 20–30 cm thick, massive, dusky red noncalcareous layer with wedge-shaped aggregate structure and slickensides (E; Css horizon in Fig. 4). This upper layer has an abrupt and wavy upper boundary overlain by thin, cross-bedded fine sandstone.

Mineralogy

The unweathered basalt consists primarily of acicular plagioclase crystals ranging from 0.5 to 1 mm long and 75 to 200 µm wide in a fine-grained groundmass of pyroxene, plagioclase, and iron-titanium oxide (Fig. 5A). Plagioclase crystals show a high degree of orientation defining a flowing banding that is parallel to over- and underlying sedimentary bedding. The basalt also contains 3 to 5 vol% (by point count) ilmenite crystals (Fig. 5A).

Basalt directly underlying the spheroidal weathering zone contains a significant amount of secondary calcite, phyllosilicate, and Fe oxide minerals (Figs. 5B–D). Isopachous calcite spar with dull luminescence lines to completely fill primary vesicles and secondary porosity within the basalt (Figs. 5B–C). In some instances, calcite fills voids formed by dissolution of plagioclase crystals (Fig. 5C). Pores incompletely filled by calcite contain botryoidal phyllosilicate precipitates (Fig. 5B), indicating that calcite precipitated first in the vesicles. Reflect light microscopy shows alteration of pyroxene and ilmenite to goethite (α-FeOOH; Fig. 5D). Phyllosilicate and iron oxide alteration products are observed along the perimeter of plagioclase laths (Fig. 5C). Phyllosilicates within calcite-filled vugs are Mg- and Fe-rich, whereas vug-filling calcite contains trace amounts of Mg and Fe. In addition, botryoidal goethite partially or entirely fills dissolution cavities developed in calcite amygdules, indicating that goethite formed subsequent to calcite under conditions that favored calcite dissolution.

X-ray diffractograms of the unweathered basalt (A in Fig. 6) reveal a sharp and intense peak at 3.21 Å, corresponding to the d(001) of plagioclase. In addition, a very broad peak near 13.7 Å indicates trace 2:1 phyllosilicates. Plagioclase peaks in the whole-rock fractions of the spheroidal weathering zone (B, C, and D in Fig. 6) show a progressive loss of intensity from the inner core-stones (B) of the spheroidally weathered zones outward through the inner (C) and outer (D) weathering rinds and upward into the overlying Css horizon (E in Fig. 6). All of these samples show relatively sharp and intense phyllosilicate d(001) peaks at ~12.65 Å. Furthermore, the outer rind of the Cr horizon (D in Fig. 6), and the Css horizon (E), exhibit minor peaks near 7.18 Å, likely indicating the presence of kandite clay (Moore and Reynolds, 1997). Both the outer weathering rind (D) and overlying Css horizon (E) exhibit low and sharp peaks at 3.33 Å and 4.26 Å, indicating the presence of quartz.
Chemical Composition

Both the whole-rock and <2 μm chemical analyses show chemical trends consistent with chemical weathering in modern soil-forming systems. Whole-rock compositions of the basalt and the basalt-weathering zone are presented in Table 1. Chemical weathering in soils preferentially removes more labile elements (e.g., alkalies) and concentrates less soluble elements such as aluminum and titanium (Monro et al., 1983). Thus, higher concentrations of more immobile elements are found toward the soil surface where chemical weathering is most intense. Variations in the major elements in the weathering profile are normalized to the immobile conservative element titanium (cf. Retallack, 1990) and presented as concentration ratios defined as:

\[
\text{concentration ratio of element} = \frac{\text{wt}\% \text{ oxide}_{(x)}}{\text{wt}\% \text{ oxide}_{(ref)} \times \frac{\text{wt}\% \text{ Ti}_{(ref)}}{\text{wt}\% \text{ Ti}_{(x)}}},
\]

where “x” denotes values within a given layer (e.g., layer E) and “ref” denotes values in the reference parent material (i.e., basalt in layer A).

In general, sodium, potassium, calcium, and phosphorus are less concentrated in the
Figure 5. Photomicrographs. (A) Plagioclase and ilmenite (opakes) crystals in host basalt. Plagioclase crystal laths show a high degree of orientation. (B) Isopachous drusy calcite (white) and phyllosilicate (center) void-fill in parent basalt. Plagioclase laths show weathering pits along perimeter of crystals. (C) Isopachous drusy calcite and calcite spar filling a vug in plagioclase basalt matrix. Some plagioclase crystals have phyllosilicate alteration rinds. (D) Ilmenite crystals (black) in plagioclase basalt (white) weathering to a latticework of fine-grained goethite (gray).

Figure 6. X-ray diffractograms of the bulk fractions of the unweathered basalt (A), the spheroidal weathering zone (B–D) and the overlying C2s horizon (E). The diffractograms are placed, from bottom to top, in order of increased weathering of the parent basalt. There is a progressive loss of plagioclase (3.21 Å and 6.48 Å) in conjunction with a gain in phyllosilicates (12.65 Å). (D) and (E) show a low and broad peak at ~7.18 Å, indicating kandite clays, and peaks at 4.27 Å and 3.33 Å that indicate quartz.
Figure 7. (A) Oriented-aggregate X-ray diffractogram of the <2 μm fraction from the parent basalt. Traces represent analyses of potassium saturation at room temperature (K⁺, 25 °C), potassium saturation and two hours heating at 500 °C (K⁺, 500 °C), magnesium saturation at room temperature (Mg²⁺), and magnesium saturation and glycerol solvation (Mg²⁺ + Glycerol). (B) Oriented-aggregate X-ray diffractogram of the <2 μm fraction from layer C. See text for details. (C) Oriented-aggregate X-ray diffractogram of the <2 μm fraction from layer D. See text for details. (D) Powder-mount X-ray diffractogram of the vesicle-filling sample Cgv. The 1.496 Å peak corresponds to the d(060) of dioctahedral montmorillonite.
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Figure 8. Powder-mount X-ray diffractogram of goethite taken from weathering profile. The Å values for the (110) and (111) peaks are reported with three decimal places from a high-resolution, long-duration X-ray analysis. The 2:1 and 1:1 phyllosilicate peaks are reported with only one decimal place due to the low and broad (00l) peaks for this analysis. The combination of peaks indicates that the sample is dominated by goethite with trace enrichment in layer D, whereas only Fe is enriched in layer D, whereas only Fe is enriched in layers C and E and the inner core-stone (B) of these samples.

TABLE 1. ELEMENTAL COMPOSITION OF FUSED GLASSES AND WT% H2O OF SAMPLES IN THIS STUDY

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size Fraction</th>
<th>Na2O</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>P2O5</th>
<th>K2O</th>
<th>CaO</th>
<th>TiO2</th>
<th>Fe2O3</th>
<th>Total wt% H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Bulk</td>
<td>4.41</td>
<td>2.48</td>
<td>19.54</td>
<td>52.85</td>
<td>0.40</td>
<td>1.67</td>
<td>7.74</td>
<td>3.45</td>
<td>6.52</td>
<td>99.06 1.18</td>
</tr>
<tr>
<td>B</td>
<td>Bulk</td>
<td>2.29</td>
<td>1.91</td>
<td>21.54</td>
<td>56.79</td>
<td>0.50</td>
<td>2.24</td>
<td>3.93</td>
<td>5.14</td>
<td>3.94</td>
<td>98.28 2.81</td>
</tr>
<tr>
<td>C</td>
<td>Bulk</td>
<td>2.35</td>
<td>2.41</td>
<td>21.77</td>
<td>51.88</td>
<td>0.52</td>
<td>2.09</td>
<td>1.71</td>
<td>4.82</td>
<td>11.03</td>
<td>98.58 3.23</td>
</tr>
<tr>
<td>Cgv</td>
<td>Bulk</td>
<td>2.25</td>
<td>3.97</td>
<td>22.51</td>
<td>61.68</td>
<td>B.D.</td>
<td>0.33</td>
<td>0.26</td>
<td>0.45</td>
<td>6.56</td>
<td>98.00 4.22</td>
</tr>
<tr>
<td>D</td>
<td>Bulk</td>
<td>1.74</td>
<td>2.51</td>
<td>24.50</td>
<td>56.15</td>
<td>0.02</td>
<td>0.73</td>
<td>1.32</td>
<td>2.62</td>
<td>9.26</td>
<td>98.85 5.41</td>
</tr>
<tr>
<td>E</td>
<td>Bulk</td>
<td>2.08</td>
<td>2.68</td>
<td>21.78</td>
<td>52.64</td>
<td>0.20</td>
<td>1.57</td>
<td>0.56</td>
<td>4.88</td>
<td>11.89</td>
<td>98.28 4.30</td>
</tr>
<tr>
<td>B</td>
<td>&lt;2 µm fraction</td>
<td>1.88</td>
<td>3.48</td>
<td>22.90</td>
<td>60.08</td>
<td>B.D.</td>
<td>0.97</td>
<td>0.71</td>
<td>2.55</td>
<td>5.78</td>
<td>98.35 4.39</td>
</tr>
<tr>
<td>C</td>
<td>&lt;2 µm fraction</td>
<td>2.06</td>
<td>3.36</td>
<td>22.54</td>
<td>59.31</td>
<td>B.D.</td>
<td>1.51</td>
<td>0.79</td>
<td>1.86</td>
<td>6.60</td>
<td>98.03 4.75</td>
</tr>
<tr>
<td>D</td>
<td>&lt;2 µm fraction</td>
<td>1.72</td>
<td>2.97</td>
<td>23.41</td>
<td>61.82</td>
<td>B.D.</td>
<td>1.51</td>
<td>0.12</td>
<td>1.11</td>
<td>7.13</td>
<td>99.79 5.23</td>
</tr>
<tr>
<td>E</td>
<td>&lt;2 µm fraction</td>
<td>1.58</td>
<td>3.07</td>
<td>22.88</td>
<td>57.91</td>
<td>B.D.</td>
<td>1.68</td>
<td>0.31</td>
<td>3.53</td>
<td>7.37</td>
<td>98.33 4.65</td>
</tr>
</tbody>
</table>

Note: B <2 µm fraction: (Ca0.01Na0.20K0.10)(Al1.40Mg0.27Fe0.33Ti0.05)(Si3.73Al0.27). C <2 µm fraction: (Ca0.02Na0.26K0.02)(Al1.33Mg0.35Fe0.30Ti0.02)(Si3.78Al0.22). Cgv: (Ca0.02Na0.26K0.02)(Al1.33Mg0.35Fe0.30Ti0.02)(Si3.78Al0.22). B.D.—concentrations below detection limits.

*Standard deviations (1σ) around the mean (n = 6).

The whole-rock fraction exhibits up-profile trends in mineral-bound water that reflect greater concentrations of secondary alteration products. There is a progressive increase in wt% H2O from the outer rind (D) of the spheroidally weathered zone (Cr horizon), in conjunction with high Al contents in the <2 µm fraction (Table 1), suggests a minor concentration of oxyhydroxide (e.g., gibbsite), unrecognized by X-ray diffraction.

Microprobe analysis of the <2 µm alteration products within the parent basalt indicates at least two different phyllosilicates—a magnesium-poor and a magnesium-rich phyllosilicate mineral (Fig. 5B; Table 2). The magnesium-poor phyllosilicate is associated with direct alteration of plagioclase feldspar crystals (Figs. 4A–C), whereas the magnesium-rich phyllosilicate occurs with other vesicle-filling minerals. High wt% FeO and TiO2 in the magnesium-poor samples suggest they probably also contain admixed oxide phases. The Mg-rich phyllosilicates are likely chlorite/smectite, or corrensite, whereas the Mg-poor phyllosilicates are probably montmorillonitic smectites. However, we were not able to calculate reasonable chemical formulas for smectite, chlorite, or chlorite/smectite minerals using the microprobe wt% oxide data. This may reflect disorder within the phyllosilicate structures or the presence of additional poorly ordered mineral phases associated with the phyllosilicates, such as Fe and Al oxyhydroxides, that were not recognized by X-ray diffraction analysis.

The kaolinite-free smectite samples in the <2 µm fraction (B, C, and Cgv; Table 1) are enriched in all cations except aluminum relative to the kaolinite-bearing smectite samples. This is not surprising, as kaolinite has only very minor substitution for Al within the octahedral sheet (Moore and Reynolds, 1997). Based on the chemical compositions of the relatively pure phyllosilicates in the <2 µm fraction, chemical formulas for samples from layers B, Cgv, and C are presented in Table 1. These chemical formulas correspond to montmorillonite. Chemical formulas for samples from layers D and E were not calculated due to the presence of kaolinite in these samples.

The <2 µm fraction has a higher wt% H2O than the corresponding whole-rock fraction for each horizon (Table 1). All of the <2 µm samples have similar wt% H2O that correspond to expected H2O yields for iron-rich montmorillonite (~4.90 wt%), with the exception of a sample from the unweathered basalt (A: 1.18 wt%) and the outer rind of the spheroidally weathered zone (D: 5.41 wt%).

The chemical composition of the goethite-rich sample Tri3g is presented in Table 3. Fe2O3.
is the dominant oxide phase with very minor concentrations of SiO₂ and Al₂O₃ in a ratio of ~2:1. This is consistent with X-ray diffraction analysis, in which goethite is the predominant crystalline phase with trace 2:1 phyllosilicates.

### Isotopic Composition

The δ¹⁸O values of calcite amygdules from the Triassic weathering profile are presented in Table 4 and Figure 4C. Calcite δ¹⁸O values are consistent throughout the profile, varying between 16.0‰ and 12.7‰.

The δ¹⁸O and δD values for the bulk and residue fractions of the goethite-rich samples are presented in Table 3. The residue remaining after goethite dissolution has more positive δ¹⁸O and δD values than the bulk fraction. The mole fraction of oxygen values in this sample was goethite. If there is some association with the goethite, it would introduce some error in the calculated X(O)Fe value. However, there is no evidence for hematite in the X-ray diffraction data. Furthermore, if the composition of the phyllosilicate associated with the Fe oxide sample is chemically similar to phyllosilicate in the overlying soil horizon, the maximum uncertainty of X(O)Fe attributed to goethite is less than one-half of one percent of the reported value in Table 3. The hydrogen isotopic composition of end-member goethite in Tri3g was determined by a mass balance calculation similar to that of the oxygen calculations, which considers the difference in the measured wt% H₂O, δD values of the bulk and residue samples, and the calculated mole fraction of hydrogen, X(H)Fe, in goethite. The end-member δ¹⁸O and δD values of Tri3g goethite are reported in Table 3 and Figure 4C.

The δ¹⁸O and δD values of phyllosilicates in the <2 μm fraction of the weathering profile and the bulk fraction of the underlying basalt are presented in Table 4 and Figure 4C. The oxygen isotopic composition of the <2 μm fraction ranges from 14.6‰ to 15.6‰ (mean value of 15.1 ± 0.5‰), which is considerably enriched over the parent basalt (δ¹⁸O = 8.2‰). The hydrogen isotopic composition of the phyllosilicates in the <2 μm fraction exhibit similar values throughout the profile, with a mean value of –74 ± 3‰.

### DISCUSSION

Spheroidal features, amygdaloidal calcites, and smectites are commonly associated with near-surface and relatively low-temperature

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**Note:** As determined from ICP-OES analyses, manometric determination of wt% H₂O in Tri3g, and Citrate-Bicarbonate-Dithionite-treated residue, measured oxygen and hydrogen isotope compositions of Tri3g and CBD residue, and calculated end-member isotopic compositions for goethite in sample. B.D.—concentrations below detection limits.
hydrothermal (e.g., Yiu and Chang, 1999) and/or meteoric weathering environments (“onion-skin weathering”; Retallack, 1990). However, the morphology, mineralogy, and chemical compositions of the uppermost weathered zone (layer E; Css horizon) that developed on the Triassic-age basalt are indicative of pedogenesis. Wedge-shaped aggregate structure and slickensides in the Css horizon are characteristic of subsurface horizons that form under seasonal soil moisture regimes (Buol et al., 1997; Soil Survey Staff, 1998). The occurrence of these features within a montmorillonite-rich matrix suggests it formed as a Vertisol (Soil Survey Staff, 1998). Vertisols typically form on flat terrain with strongly contrasted wet and dry seasonal or monsoon-type climates (Singer et al., 1994; Buol et al., 1997). Repeated wetting and drying of expandable 2:1 phyllosilicate minerals leads to shearing of plastic soil materials and slickenside formation. Vertisols require a period of soil moisture deficit and sparse vegetation in order to maintain a high concentration of basic cations, thereby preserving expandable clay minerals in the soil matrix (Duchaufour, 1982; Retallack, 1990).

The chemical composition of the weathered zone indicates a significant loss of base cations, suggesting at least a moderate degree of alteration. This degree of pedogenic weathering requires leaching of minerals within the soil, facilitated through percolating meteoric waters, similar to biaxialitization-type weathering that is predominant in winter-wet and summer-dry soils forming in Mediterranean climates (Tardy, 1971). Moreover, the clay mineral composition of the paleosol profile, in which smectite with a chemical composition similar to montmorillonite dominates, is similar to that of modern soils that form in semihumid Mediterranean climates. Trace amounts of 1:1 phyllosilicate in the outer rind of the Cr horizon (D) and the Css horizon (E) suggest soil leaching and alteration of pre-existing smectite to more stable, base-depleted kaolinite. This style of mineralogical and chemical alteration is found in Vertisols that form on stable, well-drained landscapes with relatively high rainfall (>600 mm/yr; Singer and Ben-Dor, 1987) and suggests similar conditions may have been present while the Late Triassic basalt flow underwent surficial weathering and pedogenesis. As mentioned, carbonate is present in the parent basalt and spheroidal weathering layer, but absent in the overlying Css horizon. Furthermore, there is some petrographic evidence to indicate that carbonate became undersaturated and dissolved in portions of the profile. This strongly suggests that carbonate was leached from the Css horizon as a result of increased weathering in this portion of the profile with respect to the underlying spheroidal zone and parent basalt. A study by Royer (1999) demonstrated that soil carbonate will not accumulate if precipitation exceeds 760 mm/yr. This value is in reasonable accord with the necessary amount of precipitation required for formation of kaolinite in these types of soils (Singer and Ben-Dor, 1987). Furthermore, using the geochemical clinofunction of soil alumina, soda, lime, and magnesia (Sheldon et al., 2002) in the bulk fraction of the weathered layers (Table 1) results in a calculated range of precipitation between 710 and 1080 mm/yr. By analogy with these modern data sets, rainfall was sufficiently high to leach carbonate from the paleosol profile during latter stages of weathering.

Although basaltic parent material is devoid of quartz, many soils developing on basalt contain this mineral as a result of eolian deposition of fine silt-sized grains during dry and windy episodes (Singer, 1978; Singer et al., 1994). Thus, the presence of quartz in the most highly weathered layers (D and E) of the Triassic paleosol is interpreted to indicate an eolian sediment input. In spite of the fact that precipitation was high enough to actively leach carbonate from the soil profile, the presence of eolian quartz suggests that conditions were intermittently dry.

The goethite-rich Fe oxide sample taken from below the spheroidal weathering zone (Cr) has 0% Al³⁺ substitution within the goethite lattice. This is not consistent with a soil-forming environment, in which Al³⁺ substitution is invariably higher (5–30 mol%) than that observed in this sample (Siehl and Thein, 1989). Rather, the lack of Al³⁺ in goethite suggests groundwater deposits or orestein. This goethite likely formed in the water-saturated portion of the soil or during subsequent burial. This proposed timing of goethite formation is corroborated by micromorphologic textures deduced from petrographic analysis that indicate goethite formed concomitantly with phyllosilicate formation (Fig. 5C) or soon after, occurring as a nearly monomineralic phase that replaced primary igneous oxides (Fig. 5D) or replaced preexisting calcite amygdules.

**Isotopic Inferences**

Lawrence and Taylor (1972) found that, in general, the δ¹⁸O values of the weathering products at or near Earth’s surface are significantly higher than those of volcanic parent materials due to chemical reaction with meteoric waters at relatively low temperatures. In addition, it was observed that the δD values of the weathering products may be drastically different from those found in the parent material. We observe a similar oxygen isotope enrichment of the montmorillonites relative to the parent basalt (Fig. 4C). Although paleosol phyllosilicate δD values are more positive than the parent basalt, the difference is relatively small (Table 4; Fig. 4C). The δD value of the bulk basalt likely results from secondary phyllosilicates (Fig. 6) with similar δD values to montmorillonites in the weathered layer.

The oxygen and hydrogen isotope fractionation factors estimated for smectite likely provide a reasonable representation for the phyllosilicates analyzed in this study, even though some samples also contain kaolinite (E and D). The chemical composition of the <2 μm fraction confirms that the contribution of oxygen or hydrogen from kaolinite to the bulk phyllosilicate fraction in samples D and E is very small (<5 wt%) and will not result in a measured oxygen value analytically discernable from the end-member smectite value (e.g., Savin and Lee, 1988). Therefore, smectite-water fractionations are used for paleotemperature estimates using the measured isotopic composition of the pedogenic phyllosilicates.

The δ¹⁸O and δD values of meteoric precipitation are controlled by several climatic parameters, especially temperature, “rain-out effect,” and the rain-out history of the air mass (Dansgaard, 1964). Surface weathering occurs as precipitation interacts with rock surfaces and infiltrates into the shallow subsurface. Numerous studies have documented that pedogenically derived minerals form in isotopic equilibrium with soil water, which in turn is closely related to the isotopic composition of meteoric precipitation (Lawrence and Taylor, 1971, 1972; Cerling and Quade, 1993; Yapp, 1993a). Thus, it is expected (and has been demonstrated; Yapp, 2000) that the δD and δ¹⁸O values of minerals formed at Earth’s surface will define an array roughly parallel to the meteoric water line. By inference, δD and δ¹⁸O values of the Triassic minerals may be an important source of paleoclimate information. Furthermore, if the various alteration products within this paleosol profile formed in isotopic equilibrium, then the oxygen isotopic composition of these minerals may be used to calculate the temperature at which the minerals formed.

In this study, there are five different isotopic fractionation equations that apply to calculation of ancient water δD and δ¹⁸O values and temperatures of mineralization (T in degrees Kelvin):

- Smectite-water oxygen (¹⁸O(α)) and hydrogen (¹⁰D(α)) isotope fractionation equations:

  \[
  10^\delta \ln (\alpha (\alpha)) = (2.60 \times 10^6/T) - 4.28
  \]

  \[
  \text{(Savin and Lee, 1988).}
  \]

  \[
  10^\delta \ln (\alpha (\alpha)) = (-7.50 \times 10^6/T) + 27.37
  \]

  \[
  \text{(Capuano, 1992).}
  \]
Goethite-water oxygen and hydrogen isotope fractionation equations:

\[
10^3 \ln (\delta^18O) = (1.63 \times 10^6 / T^2) - 12.3 \\
\text{(Yapp, 1990).} \tag{3}
\]

\[
\delta^16O = 0.905 \text{ (Yapp, 1987).} \tag{4}
\]

Calcite-water oxygen isotope fractionation equation:

\[
10^3 \ln (\delta^18O) = (2.78 \times 10^6 / T^2) - 2.89 \\
\text{(O’Neil et al., 1969).} \tag{5}
\]

Combination of the oxygen isotope fractionation equations for smectite, goethite, and calcite indicate that none of these minerals formed in isotopic equilibrium. This is surprising, as other work on modern soil-weathering systems (Girard et al., 2000; Yapp, 1997) and paleosols (Yapp, 1993b) suggests that isotopic equilibrium, or near-equilibrium values, should be approached by different minerals in a soil system. Isotopic data from these Triassic minerals therefore suggest formation (1) at different temperatures, (2) from waters with different isotopic composition, (3) with subsequent postpogenic alteration, or (4) a combination of these effects.

Yapp (1987, 1993a, 2000) and Delgado and Reyes (1996) proposed the following equation as a single-mineral geothermometer for smectites:

\[
3.54 \times 10^6 / T^2 = \delta^18O_{sm} - 0.125\delta^16O_{sm} + 8.95, \tag{8}
\]

where \(\delta^16O_{sm}\) and \(\delta^18O_{sm}\) are the measured smectite \(\delta^16O\) and \(\delta^18O\) values. The range of \(\delta^16O\) and \(\delta^18O\) values of the Triassic-age <2 µm fraction phyllosilicates are –78‰ to –71‰ and 14.5‰ to 15.6‰, respectively (Figs. 4B and 4C; Table 4), corresponding to a range of temperatures from 49 to 57 °C. These calculated temperatures are significantly higher than those calculated from the coexisting goethite and inconsistent with a pedogenic origin. However, the calculated water isotope \(\delta^16O\) and \(\delta^18O\) values in equilibrium with these montmorillonites range from –29 ± 4‰ to –36 ± 4‰ and –4.8 ± 0.5‰ to –5.7 ± 0.5‰, respectively. Thus, the calculated \(\delta^16O\) and \(\delta^18O\) of water in equilibrium with these phyllosilicates are, within analytical uncertainty, indistinguishable from the \(\delta^16O\) and \(\delta^18O\) values of water in equilibrium with the coexisting goethite sample.

A similar alteration history of basals has been observed in the Miocene–Early Pliocene Penghu basalts of Taiwan. Based on the \(\delta^16O\) and \(\delta^18O\) values of montmorillonitic and saponitic amygdules and fissure-fills, Yiu and Chang (1999) concluded that these minerals precipitated from meteoric groundwater or mixed groundwater and seawater under late-stage hydrothermal temperatures ranging from 20 to 50 °C. The Late Triassic Ischigualasto Formation was deposited in a closed continental basin. Therefore, seawater probably did not impact groundwater isotopic compositions. The similar calculated temperatures from the Late Triassic smectites and the Penghu basalts alteration products suggest that these deposits share a similar late-stage hydrothermal origin in the presence of meteoric waters. Furthermore, unless the measured smectite and goethite \(\delta^16O\) and \(\delta^18O\) compositions from the Late Triassic weathering profile are coincidental, such values are a strong indication that these minerals formed from the same meteoric waters with similar isotopic composition, but at different temperatures.

Although the Penghu basalts are deeply weathered, there is no significant soil development, kaolinite, or goethite associated with these deposits. However, the development of slickensides and wedge-shape aggregate structure in the Cns horizon of the Triassic weathering profile is a clear indication that soil development did take place upon and within the hydrothermally altered, smectite-rich Ischigualasto basalt flow. Montmorillonite is a common soil mineral in subtropical and temperate climates (e.g., Moore and Reynolds, 1997). Therefore, smectites that initially form in a hydrothermal environment that are subsequently incorporated into soil may not necessarily undergo mineralogical or isotopic alteration because there is no chemical force to facilitate such a change. In this regard, we consider the Triassic montmorillonites and their \(\delta^16O\) and \(\delta^18O\) values to be inherited from preexisting low-temperature hydrothermal conditions, whereas trace amounts of kaolinite found in the most weathered layers (D and E) and dissolution of carbonate may represent incipient pedogenic weathering of a hydrothermal assemblage. Furthermore, the addition of goethite to the weathering profile likely occurred subsequent to hydrothermal activity, at relatively low temperatures, penecontemporaneous with pedogenesis. We interpret the paleotemperature of 6 ± 3 °C to be near a maximum estimate of mean annual surface-air temperature during Late Triassic soil formation. This reflects that shallow subsurface temperatures are typically ~1–2 °C warmer than mean annual surface temperatures (Buol et al., 1997), and that the isotopic composition of ancient goethites has been shown to retain primary values (Yapp, 1987, 1993a, 2000).

Calcites are not amenable to single-mineral paleothermometer calculations. However, if these calcites formed from the same meteoric water \(\delta^18O\) values (~4.8‰ to ~5.7‰) associated with coexisting smectite and goethite, then the isotopic compositions of the calcites may be used to directly calculate the temperature of calcite crystallization using equation 5. The \(\delta^18O\) values of calcite amygdules from the Late Triassic weathering profile range from 12.7‰ to 16.0‰.
calcite δ¹⁸O values correspond to an approximate range of temperatures between 60 and 100 °C for calcite formation. This range of temperatures is in reasonable accord with temperatures of calcite crystallization observed in other hydrothermal systems (e.g., Clayton and Epstein, 1961).

The calculated temperatures of calcite, smectite, and goethite crystallization in the Late Triassic weathering profile correspond well with the inferred paragenetic sequence of mineral formation determined petrographically (Figs. 5A–D). In this sequence, calcite is the first mineral to form after basalt emplacement and therefore likely formed at the highest temperatures (~60–100 °C), smectite precipitation followed at lower hydrothermal temperatures (49 to 57 °C), and finally goethite precipitation at ambient Earth surface temperature (6 ± 3 °C).

Retention of Primary δD Compositions?

Numerous studies have focused on the exchangeability of oxygen and hydrogen isotopes in phyllosilicate minerals (O’Neil and Kharka, 1976; Bird and Chivas, 1988; Kyser and Kerrich, 1991; Mizota and Longstaffe, 1996). Results from both laboratory and field studies indicate that mineral hydrogen may be susceptible to postformational isotopic exchange, through the process of proton exchange, in the absence of a mineralogic or chemical change. However, Sheppard and Gilg (1996) noted serious problems with empirical evidence for low-temperature hydrogen exchange. Subsequently, Gilg (2000) made a compelling argument for the retention of original δD in Triassic through Tertiary kaolinites from southern Germany. Despite this, theoretical considerations and experimental data indicate that a <2 μm clay mineral can completely reequilibrate hydrogen isotopes at 25 °C after only a few million years (Kyser and Kerrich, 1991). Thus, the measured δD values of the Triassic phyllosilicates may reflect those of postdepositional fluids to which they were exposed.

There are no historical isotope records of meteoric rainfall near the study area. However, the measured δD and δ¹⁸O values of water from a spring (20 °C) near Ischigualasto Provincial Park are ~46‰ and ~7.3‰, respectively. These values lie upon the meteoric waterline and are likely very near the values for the weighted mean isotopic composition of meteoric rainfall and soil temperature in this area (e.g., Clark and Fritz, 1997). The corresponding δD and δ¹⁸O values for a hypothetical smectite in isotopic equilibrium with the springwaters at 20 °C are −102‰ and 18.8‰, whereas the δD and δ¹⁸O values for a hypothetical goethite are −137‰ and −0.7‰ (Fig. 9). Therefore, the measured hydrogen isotope values of the montmorillonites are 24‰–31‰ more positive, and the goethite 5‰ more positive, than the expected value for complete proton exchange with local meteoric waters. Gilg (2000) noted that it is very difficult, probably even impossible, to prove whether there has been any hydrogen isotopic exchange in phyllosilicates with younger waters. Nonetheless, these two minerals are isotopically heavier than anticipated values for proton exchange with ambient modern meteoric waters suggesting they preserve a record of preexisting, ancient conditions. Furthermore, we consider the fact that the montmorillonites and coexisting goethite apparently formed from the same meteoric waters, compelling evidence that these minerals retain Triassic hydrogen isotope compositions.

Paleoclimate Interpretation

Figure 10 presents the measured δ¹⁸O compositions of meteoric waters versus mean annual surface temperature for each site in the International Atomic Energy Association (IAEA) global database (Rozanski et al., 1993). As mentioned, the maximum range of meteoric water δ¹⁸O values in equilibrium with the Triassic minerals is ~6.9‰ to ~4.3‰. Furthermore, surface temperatures ranged from 6 ± 3 °C. Only two sites in the modern global database lie within this range of temperatures and δ¹⁸O values. These sites are Marion Island (South Pacific; ~47° S) and Lista (Norway; ~58° N). It is interesting to note that the latitudes of these modern sites are similar to the paleolatitude of the Late Triassic Ischigualasto basin (40°–50° S; Scotese and Golonka, 1992; Smith et al., 1994). These sites may serve as modern analogs for the Late Triassic climate system associated with this weathering profile. Both sites have relatively high mean annual precipitation, Marion Island with 2452 mm/yr and Lista with 1025 mm/yr. Furthermore, both of these sites occur in coastal regions, proximal to a marine-derived source of precipitation.

As noted earlier, the chemical composition of the alteration products in this weathering profile corresponds to basiallization weathering in modern soils (Tardy, 1971) with a calculated precipitation range between 710 and 1080 mm/yr (cf. Sheldon et al., 2002). However, if this deposit represents incipient pedogenic overprinting of a hydrothermal deposit, the
elemental composition of weathering products may not represent a low-temperature soil-forming environment. Rather, the elemental and mineralogical composition of this deposit may be more representative of a relief hydrothermal system that never reached chemical equilibrium with the soil-forming environment. Therefore, soil geochemical climafunctions may result in erroneous paleoclimate reconstructions for this weathering system.

Pedogenically derived kaolinite and dissolution of carbonate from the Triassic paleosol profile suggest precipitation exceeded 760 mm/yr. This conforms to precipitation values inferred from modern sites with similar surface air temperatures and isotopic ranges of meteoric waters calculated from the Triassic minerals. However, the smectite and goethite isotopic data in this weathering profile suggest that precipitation may have been >1000 mm/yr, higher than values inferred by carbonate dissolution (Royer, 1999) and geochemical transfer functions (Sheldon et al., 2002). Stable isotope evidence, in conjunction with a Vertisol paleosol morphology, suggests a quite humid and cool climate characterized by seasonal precipitation during deposition of the Late Triassic, lower Ischigualasto Formation.

CONCLUSIONS

Integrated field, mineral, chemical, and stable isotope analysis of a weathered horizon developed on Carnian-age basalt in the Ischigualasto basin, northwest Argentina, indicates a pedogenic origin. The presence of wedge-shaped aggregate structure and slickensides indicate it was a Vertisol that formed on a well-drained landscape with seasonal soil moisture conditions. Loss of carbonate and incipient development of kaolinite in the soil profile suggest precipitation may have been in excess of 760 mm/yr. Quartz in the paleosol profile may record episodes of eolian deposition in the basin.

Chemical trends within the paleosol profile are consistent with those observed in modern weathering profiles from seasonal, subhumid climates. Despite this, none of the authigenic minerals from the weathering profile exhibits isotopic equilibrium, which is not consistent with a pedogenic origin. However, on the basis of the combined δD and δ18O values, these minerals apparently formed from meteoric waters of a similar isotopic composition (maximum range: δD = −24‰ to −45‰, δ18O = −4.3‰ to −6.9‰), but at very different temperatures. Calcite and montmorillonite may have formed over a range of temperatures from 60 to 100 °C and 49 to 57 °C, respectively, during waning stages of hydrothermal alteration, whereas goethite formed at 6 ± 3 °C during supergene, or pedogenic, weathering. Modern regions with similar isotopic compositions of meteoric water and earth-surface temperatures are characterized by rainfall in excess of 1000 mm/yr and may indicate similar conditions for the Late Triassic Ischigualasto-Villa Unión basin.

The paragenetic sequence of hydrothermal to supergene weathering in this basin flow is complex and may be representative of a general phenomenon in continental rift basalts. Despite these complications, this study shows great potential for these geologically abundant lithologies as records of paleoclimate.

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