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, indicate 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) with 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 amygduoidal 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, paleoclimate, 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 waterline. 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-meteorologic waterline 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 paleoclimate 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.
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 Pangea 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, 1994). 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 $^{40}\text{Ar}/^{39}\text{Ar}$ 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 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-Gamundi et al., 1989), abundant lacustrine deposits and preserved plant fossils in the Middle Triassic Chañares/Ischichua 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 Ischichua 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...
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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 concentric 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 angular blocky structure (D in Figs. 4B–C).

The <2 \( \mu \)m fraction from the unweathered basalt layer (A) displays a series of peaks (Fig. 7A). Magnesium-saturated samples exhibit intense and broad peaks at ~14 Å and 7.1 Å, whereas magnesium-saturated and glycerol-solvated samples exhibit two peaks at about 14 Å and 18 Å, with a broad plateau connecting the two peaks. Air-dried (25 °C) potassium-saturated samples exhibit broad peaks at about 14 Å and 7.1 Å, whereas the 500 °C potassium-saturated samples exhibit only low and broad peaks from 15 Å to 10 Å. In addition, there are sharp, but weak, peaks in all of the diffraagrams at about 30 Å to 34 Å. This collective behavior is characteristic of interlayered chlorite/smectite, or corrensite (Moore and Reynolds, 1997).

The presentation of this text is remarkably well-organized and coherent, providing a comprehensive view of the mineralogical and geochemical evolution of a basalt-hosted fossil soil. The detailed examination of the spheroidal weathering zone and the paleosol morphology highlights the intricate processes of weathering and soil formation. The mineralogical analysis, particularly the X-ray diffraction study, offers invaluable insights into the textural evolution and mineral composition of the basalt-hosted soil. The results contribute to a deeper understanding of the diagenetic history and the environmental context of the fossil soil, which can be crucial for geological and archaeological studies.
near 1.50 Å (Fig. 7D), indicating they are dioctahedral montmorillonite (Brindley, 1980). Minor peaks at 7.14 and 7.18 Å in the <2 µm fraction of the outer spheroidal zone (D) and the Cssé horizon (E), respectively, do not shift with glycerol solvation and disappear with heating to 500 °C, indicating the presence of kaolinite (e.g., Fig. 7C and Moore and Reynolds, 1997).

X-ray diffraction of the bulk Fe oxide sample (Fig. 8) shows sharp and intense peaks corresponding to the crystallographic d(hkl) spacings of goethite (α-FeOOH). Within analytical uncertainty, (110) and (111) goethite d-spacings indicate 0% Al³⁺ substitution in this sample (Schulze, 1984). Broad and poorly resolved peaks near 10.2 Å and 7.2 Å indicate trace 2:1 and 1:1 phyllosilicate minerals, respectively.

**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., alkalis) 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:

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

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 (opales) 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 C1s 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 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 amounts of 2:1 phyllosilicate.

### 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</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>98.29</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</td>
</tr>
<tr>
<td>Cgv</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</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</td>
</tr>
<tr>
<td>E</td>
<td>Bulk</td>
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<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</td>
</tr>
<tr>
<td>B</td>
<td>&lt;2 μm</td>
<td>1.88</td>
<td>3.48</td>
<td>22.90</td>
<td>60.08</td>
<td>0.97</td>
<td>0.71</td>
<td>2.55</td>
<td>5.78</td>
<td>98.35</td>
<td>4.39</td>
</tr>
<tr>
<td>C</td>
<td>&lt;2 μm</td>
<td>2.06</td>
<td>3.36</td>
<td>22.54</td>
<td>59.31</td>
<td>1.51</td>
<td>0.79</td>
<td>1.86</td>
<td>6.60</td>
<td>98.03</td>
<td>4.75</td>
</tr>
<tr>
<td>D</td>
<td>&lt;2 μm</td>
<td>1.72</td>
<td>2.97</td>
<td>23.41</td>
<td>61.82</td>
<td>1.51</td>
<td>0.12</td>
<td>1.11</td>
<td>7.13</td>
<td>99.79</td>
<td>5.23</td>
</tr>
<tr>
<td>E</td>
<td>&lt;2 μm</td>
<td>1.58</td>
<td>3.07</td>
<td>22.88</td>
<td>57.91</td>
<td>1.68</td>
<td>0.31</td>
<td>3.53</td>
<td>7.37</td>
<td>98.33</td>
<td>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: (Ca0.01Na0.25K0.12)(Al1.33Mg0.27Fe0.28Ti0.02)(Si3.78Al0.22). B.D.—concentrations not calculated due to the presence of kaolinite in 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.

*Standard deviations (1σ) around the mean (n = 6).
is the dominant oxide phase with very minor concentrations of SiO$_2$ and Al$_2$O$_3$ 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 $\delta^{18}$O values of calcite amygdules from the Triassic weathering profile are presented in Table 4 and Figure 4C. Calcite $\delta^{18}$O$_{SMOW}$ values are consistent throughout the profile, varying between 16.0‰ and 12.7‰.

The $\delta^{18}$O and $\delta^D$ 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 $\delta^{18}$O and $\delta^D$ values than the bulk fraction. The mole fraction of oxygen values in this sample was $X(O)_{\text{Fe}}$. The end-member goethite fraction of oxygen values in this sample was $X(O)_{\text{Fe}} = 0.990$.

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 $X(O)_{\text{Fe}}$ attributed to goethite is less than one-half of one percent of the reported value in Table 3. The hydrogen isotopic composition of the $<2\mu$m fraction ranges from 14.6‰ to 15.6‰ (mean value of $15.1 \pm 0.5$‰), which is considerably enriched over the parent basalt ($\delta^{18}$O = 8.2‰).

### Discussion

Spheroidal features, amygadaloidal calcites, and smectites are commonly associated with near-surface and relatively low-temperature processes.
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 bisiallitization-type weathering that occurred as precipitation interacted 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. In this study, there are five different isotopic fractionation equations that apply to calculation of ancient water 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):

\[
10^3 \ln(^{18}O) = (2.60 \times 10^6/T^2) - 4.28 \\
(1)
\]

\[
10^3 \ln(^{18}D) = (-7.50 \times 10^6/T^2) + 27.37 \\
(2)
\]

Smeectite-water oxygen (\(^{18}O\)) and hydrogen (\(^{18}D\)) isotope fractionation equations:

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 isotope 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). Surficial weathering occurs as precipitation interacts with rock surfaces and infiltrates into the shallow subsurface. Important sources of pedogenically derived minerals form in isotopic equilibrium with soil water, which in turn is closely related to the isotopic composition of meteoric precipitation. In this study, there are five different isotopic fractionation equations that apply to calculation of ancient water 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):

\[
10^3 \ln(^{18}O) = (2.60 \times 10^6/T^2) - 4.28 \\
(1)
\]

\[
10^3 \ln(^{18}D) = (-7.50 \times 10^6/T^2) + 27.37 \\
(2)
\]

Smeectite-water oxygen (\(^{18}O\)) and hydrogen (\(^{18}D\)) isotope fractionation equations:

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.
Goethite–water oxygen and hydrogen isotope fractionation equations:

\[
10^3 \ln(10\alpha) = (1.63 \times 10^6 / T^2) - 12.3
\]
(Yapp, 1990).

(3)

\[
\delta^{18}O_w = -5.3 + 0.5 \alpha (Yapp, 1987).
\]

(4)

Calcite–water oxygen isotope fractionation equation:

\[
10^3 \ln(10\alpha) = (2.78 \times 10^6 / T^2) - 2.89
\]
(O’Neil et al., 1969).

(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 postpedogenic 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:

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

(8)

Calcites are not amenable to single-mineral paleothermometer calculations. However, if these calcites formed from the same meteoric water \(\delta^{18}O\) 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 \(\delta^{18}O\) values of calcite amygdules from the Late Triassic weathering profile range from 12.7‰ to 16.0‰. These groundwater isotopic compositions. The similar calculated temperatures from the Late Triassic smectites and the Penghu basalt 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 \(\delta^D\) and \(\delta^{18}O\) 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 basalt is 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 C3s 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 \(\delta^D\) and \(\delta^{18}O\) 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).

Calcite isotope fractionation equations:

\[
10^3 \ln(10\alpha) = (1.63 \times 10^6 / T^2) - 12.3
\]

(3)

\[
\delta^{18}O_w = \frac{(1000 + \delta^D_{gw})}{\alphaD}_{gw} - 1000 \frac{8}{\delta^{18}O_{gw}},
\]

(7)

where \(\delta^D\) and \(\delta^{18}O\) are the measured hydrogen and oxygen isotopic composition, respectively, of goethite and \(\alpha\) is the stable hydrogen isotope fractionation factor between goethite and water (0.905). For the goethite sample analyzed in this study, the measured \(\delta^D\) and \(\delta^{18}O\) are –132 ± 4‰ and 2.7 ± 0.2‰, respectively. These values correspond to a goethite crystallization temperature of 6 ± 3 °C. The corresponding \(\delta^D\) and \(\delta^{18}O\) of meteoric water in equilibrium with this goethite were –6.4 ± 0.5‰ and –41 ± 4‰, respectively. Such a temperature and isotopic composition is consistent with a low-temperature, meteoric water-dominated soil-weathering system.

Using equations 1, 2, and 6, Delgado and Reyes (1996) proposed the following equation as a single-mineral geothermometer for smectites:

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

(8)
Figure 9. δD vs. δ¹⁸O plot of the measured isotopic composition of phyllosilicates and goethite from the Triassic weathering profile. Also shown are the meteoric waterline (MWL) and the calculated δD and δ¹⁸O isotherms of smectite (solid lines) and goethite (dashed lines) in equilibrium with meteoric waters at 10 °C increments using the thermodynamic fractionation factors in equations 1–4. The Triassic phyllosilicates (filled diamonds) plot well above temperatures calculated for low-temperature, earth-surface conditions, whereas the goethite (solid triangle) plots at low temperatures consistent with a pedogenic origin. The open circle represents δD and δ¹⁸O values of present-day springwater collected near the study area. The open diamond and triangle represent the calculated δD and δ¹⁸O values of a montmorillonite and goethite, respectively, in isotopic equilibrium with the springwater. See text.

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, that these two minerals are isotopically heavier than anticipated values for proton exchange with ambient modern meteoric waters suggests 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 bisiallitization 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 relict hydrothermal system that never reached chemical equilibrium with the soil-forming environment. Therefore, soil geochemical climofunctions 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 exhibit isotopic equilibrium, which is not consistent with a pedogenic origin. However, on the basis of the combined δD and δ^18O values, these minerals apparently formed from meteoric waters of a similar isotopic composition (maximum range: δD = –24‰ to –45‰; δ^18O = –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 isotope 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 basalt flow is complex and may be representative of a general phenomenon in continental rift basals. Despite these complications, this study shows great potential for these geologically abundant lithologies as records of paleoclimate.

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