Metonic fluid infiltration in the Argentine Precordillera fold-and-thrust belt: Evidence from H isotopic studies of neoformed clay minerals

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ABSTRACT

Fluids in the upper crust can affect the strength properties, composition, and mineralization of rock units, but the source(s) of these fluids and their transport during deformation are not well understood. Stable isotopic studies of clay-rich rocks, particularly newly formed illitic clays, shed light on the source of geofluids involved during faulting and folding. Hydrogen isotopic (δD) measurements of fault gouge and folded clay-rich sediments from the Argentine Precordillera show meteoric, surface-sourced fluid involvement during Miocene faulting. The δD composition of neoformed clay minerals is between ~70‰ and ~90‰ ± 2‰. The associated composition of fluids ranges from ~57‰ to ~72‰ ± 10‰, matching values for a surface-derived source. Regional Miocene meteoric fluid infiltrated into the evolving fold-and-thrust belt, accumulated in basin sediments, and was subsequently expelled by the overriding rock units during late Miocene shortening. A systematic increase in δD signature with deformation age is preserved that matches regional climatic changes during late Miocene aridification, cooling, and glacial expansion.

INTRODUCTION

Fluid migration through Earth’s crust plays a major role in the structural and chemical evolution of rock units. Fluids transport both heat and mass, resulting in the generation of secondary mineral species, including ores, veins, and, the focus of this paper, clay minerals. Through studies of secondary minerals, it has been determined that fluids penetrate fault zones, as far down as the brittle-plastic transition (Kerrich et al., 1984; Gébelin et al., 2014; Menzies et al., 2014). Sibison (1994) was among the first to describe the dynamic interactions between faulting and fluid flow, noting that fault-related crustal stresses can cause fluid redistribution and, following on earlier work (Hubbert and Rubey, 1959; Byerlee, 1993; Muir-Wood and King, 1993), that fluids promote faulting by modifying the stress state of the crust. Additionally, stress reorganization during faulting can cause both dilatancy and overpressurization in the fault zone, allowing faults to act as conduits for fluids that are pumped through the crust during earthquake cycles (Muir-Wood and King, 1993; Sibson, 1994; Caine et al., 1996; Evans et al., 1997; Aydin, 2000; Faulkner et al., 2010).

Fluids moving through fault zones leave behind a record of their passage by chemically altering the host rock, yielding both transformed and neoformed minerals, including metasomatic mineral species, veins, and ores (Kerrich, 1986; Taylor, 1974; Micklethwaite et al., 2014). Many shallow-crustal faults develop clay-rich gouge during cataclastic deformation and mineralogical transformations associated with fluid flow (Engelder, 1974; Chester and Logan, 1987; Vrolijk and van der Pluijm, 1999; Haines and van der Pluijm, 2012). The chemical and stable isotopic composition of neoformed minerals can be used to probe the chemistry and origins of the geofluids from which they grew (Taylor, 1974).

Previous research in the area of geofluid sourcing has focused on secondary minerals in veins, ores, and fault rock for chemical and isotopic study. For example, secondary white mica in North American extensional fault systems has been the subject of stable isotopic studies that aim to constrain the origin of fluids that are active deep in the crust (Fricke et al., 1992; Mulch et al., 2004; Gébelin et al., 2011, 2014; McFadden et al., 2015). These studies have indicated that meteonic fluids play a large role in detachment faults down to the brittle-plastic transition. In contrast, studies of clay minerals and veins formed in association with contractional fault systems have suggested input from deeper, metamorphic or magmatic fluids (Bradbury and Woodwell, 1987; Templeton et al., 1998; Uysal et al., 2006; Rossi and Rolland, 2014). This study aims to probe the origin of fluids in fold-and-thrust belts, which represent complex tectonic settings with protracted tectonic histories and complex geologies and deformation styles.

FLUIDS IN FOLD-AND-THRUST BELTS

Hypotheses for geofluid sources and pathways in fold-and-thrust belts have implications for the dynamic evolution of mountain belts and fluid driving forces. End-member sources include surface-derived fluids (meteoric, formational) at one end and deeply sourced (metamorphic) fluids at the other, as illustrated in Figure 1. Fluid pathways and flow velocity depend on a variety of factors, including rock porosity and permeability, as well as thermal and pressure gradients (Ge and Garven, 1994; Lyubetskaya and Ague, 2009; Faulkner et al., 2010; Pollyea et al., 2015). Deformation in orogenic belts has the potential to increase permeability and porosity of the rock units through fracturing and faulting (Koons et al., 1998; Faulkner et al., 2010), while topography can provide a hydraulic head.
(Koons and Craw, 1991; Deming, 1994; Garven, 1995). Each of these processes has the effect of promoting flow of higher-elevation, hinterland-sourced meteoric water toward the foreland fold-and-thrust belt and foreland basin. Deep burial of rock during orogeny increases pressure and temperature, resulting in prograde metamorphic dehydration reactions, which release associated metamorphic fluids (Bradbury and Woodwell, 1987; Ferry, 1988; Koons and Craw, 1991; Templeton et al., 1998). These increased pressure-temperature conditions instead promote the upward flow of deeply sourced geo-fluids, which migrate toward lower-pressure and lower-temperature conditions near the surface. Thrust sheet loading, sediment compaction, and pore space reduction may further promote the migration of fluids from the hinterland toward the foreland, expelling formational fluids, which may be either oceanic or meteoric in primary origin (Taylor, 1974; Sheppard, 1986; Oliver, 1986; Machel and Cavell, 1999).

Different fluid source reservoirs have characteristic physical and chemical properties. Surface-sourced meteoric fluids are generally low in temperature and salinity, whereas deeply sourced metamorphic fluids are higher in temperature and salinity (Yardley and Bodnar, 2014). Formational fluids also tend to be higher in salinity, but they have more moderate temperatures and are commonly associated with hydrocarbons, unlike meteoric and metamorphic fluids (Yardley and Bodnar, 2014). Notably, deeply sourced, high-temperature fluids, as opposed to surface-derived, low-temperature fluids, have distinct stable isotopic compositions of both hydrogen and oxygen (Taylor, 1974; Sheppard, 1986). Past geofluid studies have successfully exploited these differences, often using fluid inclusions to understand fluid chemistry and trapping temperature during fluid flow and vein formation (Evans and Battles, 1999; Barker et al., 2000; Lacroix et al., 2014). For example, Evans and Battles (1999) conducted a comprehensive study of fluid inclusion chemistry and oxygen isotopes in veins, revealing episodic fluid flow in the stratigraphy of the Appalachian foreland. In the Pyrenees, stable isotopic studies of primary, syn-, and postorogenic veins also pointed to a complicated history of fluid origin and migration, with composition of fluids varying through time and space (Travé et al., 2007; Lacroix et al., 2014). In the Sevier fold-and-thrust belt of North America, vein oxygen isotope studies revealed fluid of mixed origins as well (Bebout et al., 2001; Anastasio et al., 2004; Vandeginste et al., 2012). Though these studies have elucidated a range of sources and pathways of orogenic fluids, they have limitations. First, veins are typically difficult to date, and their sequence of formation relies on interpretation of vein geometry and morphology. Similarly, the timing of fluid inclusions (whether primary or secondary) also depends on interpretations of vein morphology. Additionally, fluid inclusions can leak during deformation, potentially losing the primary chemical composition of fluids (e.g., Kendrick and Burnard, 2012). Last, the isotopic work of most studies relies on oxygen isotopes, which have been shown to buffer with host rock, losing potential far-field source signals and thus decreasing their general utility in determining fluid sources (Ghisetti et al., 2001; Clauer et al., 2013; Rossi and Rolland, 2014). Whereas oxygen is ubiquitous in earth materials, hydrogen is an uncommon element in most minerals, except clays and hydrocarbons, and thus it has the potential to reliably preserve far-traveled fluid source signatures. For example, Fitz-Diaz et al. (2014) used hydrogen isotopes in secondary clay minerals along with fluid inclusions and veins to study fluid sources in the Mexican fold-and-thrust belt, concluding that fluid source mixing played an important role during thrusting. Boles et al. (2015) examined the hydrogen composition of illitic clay in North Anatolian fault rocks, concluding that meteoric fluid infiltrated the crust during deformation. Additionally, Haines et al. (2016) looked at hydrogen isotopic signatures of neoformed clay minerals from low-angle normal faults in the Basin and Range and linked their composition to the downward infiltration of meteoric waters into the subsurface. These studies demonstrated that the hydrogen isotopic composition of neoformed clay minerals can be a useful tool for geofluid studies in the upper crust.

Here, we present new hydrogen isotope results from neoformed clay minerals in the Precordillera fold-and-thrust belt of Argentina. This area was targeted for study due to the abundance of well-exposed clay-rich fault gouge and a well-constrained chronology of fault motion (e.g., Beer, 1990; Jordan et al., 1993; Alvarez-Marron et al., 2006; Allmendinger and Judge, 2014; Fosdick et al., 2015). Our results show that surface-derived fluids played a significant role in the evolution of this fold-and-thrust belt. We also use the results to examine the influence of changing climate or elevation on the isotopic composition of surface-sourced geofluids in the Precordillera during the late Miocene.

**GEOLOGIC SETTING**

**Central Andes**

The southern Central Andes of Chile and Argentina are divided into several structural domains: the Coastal Cordillera, the Principal Cordillera, the Frontal Cordillera, the Precordillera, and the Sierras Pampeanas (Fig. 2A; Ramos, 1988; Ramos et al., 2002). The Coastal Cordillera is interpreted as a deformed and metamorphosed accretionary wedge that formed in the middle Paleozoic following the accretion of the Chilenia terrane (Herve et al., 1982, in Ramos, 1988). The Principal Cordillera is composed primarily of Mesozoic and Cenozoic volcanic units that make up the core zone of the Andes around 30°S. The Frontal Cordillera lies just to the east of the Principal Cordillera, consisting of faulted and deformed Paleozoic and Mesozoic rocks, including the Permian–Triassic Choiyoi Formation, which is composed primarily of granitoids and rhyolites (Kay et al., 1989). The Precordillera is a thin-skinned foreland fold-and-thrust belt that deforms Paleozoic to Cenozoic units and extends eastward from the Frontal Cordillera to the Bermejo Basin (Jordan et al., 1993; Ramos et al., 2002). Further east, the Sierras Pampeanas protrude from the foreland basin in a series of
The occurrence of oppositely verging, thin- and thick-skinned components of deformation in the foreland creates a triangle zone in the basin that is bounded on the east and west by thrust faults, steep, west-vergent thrusts (Ramos et al., 2002). The lack of volcanic activity in the Main and Frontal Cordillera has been attributed to flat-slab subduction of the Nazca plate below the South American plate, which began around 20 Ma with the subduction of the Juan Fernández Ridge (Ramos et al., 2002). Neogene fault activity in the Precordillera fold-and-thrust belt also began around this time (Jordan et al., 1993; Fosdick et al., 2015). This is evidenced by sedimentation patterns in the Bermejo foreland as well as crosscutting and onlapping relationships, with earliest thrusting beginning at 21.6 ± 0.8 Ma and the majority of shortening occurring in the last 16 m.y. (Jordan et al., 1993). Recent thermochronologic studies have largely confirmed this timing of deformation (Fosdick et al., 2015). The well-constrained timing of deformation and extensive exposure of this fold-and-thrust belt make the Argentine Precordillera an ideal place in which to study orogenic fluid dynamics (Jordan et al., 1993; Alvarez-Marron et al., 2006).

Precordillera Fold-and-Thrust Belt

The Argentine Precordillera fold-and-thrust belt is located in the southern Central Andes of northwestern Argentina between ~28°S and 33°S latitude (Fig. 2B). Its protracted tectonic history began with a major period of rifting at ca. 600 Ma, which resulted in the formation of a carbonate platform bounded on its western edge by continental slope facies and oceanic crust (Ramos, 1988). The initiation of subduction during Ordovician and Early Devonian times is indicated by arc magmatism that is manifested in the western Sierras Pampeanas (Ramos, 1988). This volcanic arc was extinguished following the collision of the Chilena terrane with the continental margin in the end-Devonian, which also caused the uplift and subaerial exposure of the carbonate platform units and the obducted ophiolitic units in an east-vergent thrust stack (Ramos, 1988; Alvarez-Marron et al., 2006). This episode of Paleozoic compression, which has been recognized and described by many authors (e.g., von Gosen, 1997; Alvarez-Marron et al., 2006), created the structural setting upon which more recent deformation is superimposed.

Miocene to present deformation in the Precordillera, referred to as the Andean orogeny, is responsible for the current configuration of the thrust sheets, mountain belts, and intervening basins (Ramos, 1988). Along the Jáchal River, the Precordillera is composed of six major thrust faults: From west to east, these are the Tranca, Caracol, Blanco, Blanquitos, San Roque, and Niquivil thrusts. These six faults place Paleozoic marine clastics and carbonates over Miocene–Pliocene continental sedimentary units (Allmendinger and Judge, 2014). The area can be divided into two regions based on the geology of the hanging-wall units. The two westmost thrusts, Tranca and Caracol, expose the Ordovician Yerba Loca Formation, a deep-water turbidite horizon, whereas the eastern thrust sheets, Blanco, Blanquitos, and San Roque, bring Ordovician San Juan limestone and overlying formations to the surface (Allmendinger and Judge, 2014). This is evidenced by sedimentation patterns in the Bermejo foreland as well as crosscutting and onlapping relationships, with earliest thrusting beginning at 21.6 ± 0.8 Ma and the majority of shortening occurring in the last 16 m.y. (Jordan et al., 1993). Recent thermochronologic studies have largely confirmed this timing of deformation (Fosdick et al., 2015). The well-constrained timing of deformation and extensive exposure of this fold-and-thrust belt make the Argentine Precordillera an ideal place in which to study orogenic fluid dynamics (Jordan et al., 1993; Alvarez-Marron et al., 2006).
Thrusting is thin skinned in character and dies out to the east, resulting in a series of synclines and anticlines that warp the stratigraphy of the Bermejo Basin. Though activation on some faults likely overlapped in time, thrusting generally proceeded from west to east, but also with instances of reactivation occurring in the Tranca and Caracol fault zones, as evidenced by thrusting within Tertiary-aged conglomerates that flank the valley walls (Jordan et al., 1993; Fosdick et al., 2015). The Talacasto thrust is situated just south of the well-studied Jáchal River section of the Precordillera, and it is exposed along Provincial Route 436. It too places Ordovician San Juan limestone on top of Neogene siliciclastics and is structurally correlated with the San Roque fault to the north. A recent stratigraphic study of both volcanic and detrital zircon ages and apatite (U-Th)/He thermochronology from the bounding Talacasto basin sediments indicated that the age of thrusting in this area was coeval with major episodes of thrusting in the northern sections of the Precordillera (ca. 12–9 Ma; Levina et al., 2014; Fosdick et al., 2015). Incorporating this southern area in with the main transect provides regional context for fluid involvement in faulting. The frontal thrusts in the Precordillera are still actively deforming due to the continued subduction of the Nazca plate below the western margin of South America (Ramos et al., 2002). With fault activity extending from the present back through the early Miocene, 8D signatures of neoformed clay minerals in the Precordilleran thrusts have the potential to record the sources of the fluids involved in thrusting and their potential evolution through time.

**METHODS**

**Sampling Strategy and Sample Preparation**

Fault gouge samples in the Precordillera fold-and-thrust belt were collected in the San Juan Province of Argentina. Samples were taken from several major thrust faults in the area of the Jáchal River, along National Route 150 between Rodeo and San José de Jáchal and also along Provincial Route 436 between the junction of Route 40 and Route 149 (Table 1; Fig. 2). At each fault outcrop, samples were taken from visibly distinct zones in the fault gouge as defined by variations in fault rock texture and color (Fig. 3). One sample, Tala-F, was taken from a folded clay-rich horizon within the San Juan Formation near the Talacasto thrust front.

Clay-rich rock samples were gently disaggregated by hand using an agate mortar and pestle in the clay laboratory at the University of Michigan. Disaggregated samples were suspended in...
The gouge samples were then separated by high-speed centrifugation according to Stoke’s law in a Thermo Scientific CL-2 centrifuge. Gouge samples were divided into five clay-sized fractions (fine: <0.05 μm, medium-fine: 0.05–0.2 μm, medium: 0.2–0.5 μm, medium-coarse: 0.5–1 μm, and coarse: 1–2 μm).

Size fractions were prepared for characterization by X-ray diffraction (XRD). First, we use oriented clay mounts for detailed clay mineral identification. Approximately 300 mg of each of the clay size fraction were suspended in 5 mL of deionized water and deposited onto glass slides using a dropper in accordance with the suspension method detailed by Moore and Reynolds (1997). Samples were left to dry in an oven at 50 °C for ~1–2 h. Powder mounts of size fractions were prepared for quantitative XRD polytype analysis using a top-loading, razor-tamping method to promote randomness of mineral orientation (Moore and Reynolds, 1997; Zhang et al., 2003).

**X-Ray Diffraction**

Each oriented clay size fraction was scanned from 2° to 30° 2θ using a copper source Rigaku Ultima IV XRD at an accelerating voltage of 40 kV and filament current of 44 mA at a speed of 1°/min with a nickel-foil K-beta filter installed. Oriented slides increase the intensity of the clay mineral basal peaks, which are the most diagnostic for identifying clay phases. In order to identify expandable clay species (e.g., smectite and vermiculite), each oriented clay slide was placed in a glass desiccator with liquid ethylene glycol and heated in an oven at 50 °C for at least 8 h prior to XRD analysis. Glycolated samples were then rescanned under the same X-ray conditions as described already. Random powder mounts were also scanned under the same machine conditions from 2° to 80° 2θ at a speed of 0.3°/min to obtain high-resolution X-ray patterns. High-resolution patterns allow for the quantification of clay mineral polytypes, which are key factors in identifying the distinction between detrital and neoformed clay species.

**Clay Mineral and Polytype Quantification**

Semi-quantitative clay mineral proportions were calculated using the mineral intensity factor (MIF) method as outlined by Moore and Reynolds (1997). MIF uses the relative intensities of clay mineral basal reflections in order to quantify their relative proportions. For the calculation, peaks of each clay mineral species in a small 2θ range are chosen for comparison. We used the illite 002, chlorite 003, and, when present, smectite 003 peaks for our calculation. The integrated intensity of each peak is then compared to published mineral reference intensities (MRIs) of these peaks, which take into account mineral diffraction properties (Moore and Reynolds, 1997). Mineral proportion determinations are calculated by normalizing the intensities relative to an internal reference peak, in our case illite 003. The accuracy of this calculation is approximately ±5% (Moore and Reynolds, 1997). Whereas the MIF method can be used to distinguish between different clay species (e.g., illite and chlorite) by comparing the different basal reflection peaks that are unique to each clay mineral, it cannot distinguish between different polytypes of the same clay species (e.g., 1Md illite and 2M1 illite) that have the same basal peaks, which are key features in our application. All polytypes of illite have the same 001 reflections, but because of variable sheet stacking sequences, they have different nonbasal hkl peaks.

To determine the variation in illite polytypes between samples and size fractions, we used the end-member standard matching method described in Haines and van der Pluijm (2008). The 2M1 polytype of illite is a highly ordered, high-temperature mica polytype, which, in fault gouge, is detrital in origin, whereas the 1Md polytype is a low-temperature, disordered polytype that is authigenically formed (Vrolijk and van der Pluijm, 1999). Standards of monomineralic 2M1 illite (Owl Creek Muscovite) and 1Md illite (Clay Mineral Society standard 1Mt-1 illite) were prepared, and random powder mounts of each were scanned using identical machine parameters along with the sample random powder mounts. Standard XRD patterns were input into a spreadsheet and mathematically mixed in various proportions to closely match the patterns of the samples (Fig. 4). Visual matching focuses on polytype specific (hkl) peaks and the shape of the XRD pattern baseline, minimizing match errors; the polytype quantification error is ±2%–3% (Haines and van der Pluijm, 2008).

**Authigenic (1Md) Calculation**

The proportion of authigenic 1Md illite was calculated from the results of the MIF and standard matching analyses. Multiplying the proportion of total illite by the proportion of the illite of the 1Md polytype gives the total proportion of 1Md illite in each sample. Pairing the error of polytype quantification with that of δD measurements (±2‰–3‰), we used a York-style regression to determine the δD composition of the 1Md authigenic end-member illite (York, 1968). This regression method offers a more robust error analysis than standard regression analysis by incorporating individual errors in both polytype and δD quantifications.

**Hydrogen Isotopic Analysis**

Five samples that span the spatial and temporal deformational activity of the Prelodilla (Fig. 2B) were divided into size fractions for hydrogen isotopic analysis. The Caracol West fault sample (CW-2) was taken from the western side of the study area (Fig. 2B), where continental slope facies of the Ordovician Yerba Loca formation are thrust atop Neogene basin sediments. Movement on this fault occurred between ca. 22–19 Ma and 16–13 Ma (Jordan et al., 1993). Samples from the Blanquitos (sample BQ-R) and San Roque thrusts (sample SRN-2) were taken in the eastern region of the Precordillera. These faults were active ca. 12–10 Ma and 11–2 Ma, respectively, and both place Ordovician San Juan limestone on top of Neogene siliciclastics (Ragona et al., 1995; Jordan et al., 1993; Allmendinger and Judge, 2014). The Talacasto thrust is structurally correlated with the San Roque thrust and outcrops ~100 km to the south of the San Roque sample outcrop. Two samples were collected, one sample from the fault zone (Talca-1b), as well as one sample from a clay-rich horizon within the hanging wall ~0.5 km from the fault outcrop (Tala-F). This fault also places Ordovician carbonates atop Neogene basin sediments and is thought to have been active from ca. 12 to 9 Ma (Levina et al., 2014). H isotope measurements were completed on a Thermo Finnigan MAT 253 mass spectrometer coupled to a high-temperature conversion elemental analyzer (TC-EA) at the Biodiversität und Klima Forschungszentrum (BiK-F) Stable Isotope Laboratory in Frankfurt, Germany. Approximately 1 mg of each size fraction, one duplicate from each sample, and laboratory standards were individually encased in gold foil and kept overnight under vacuum at 200 °C. Samples were transferred to a zero-blank autosampler that was purged with helium gas to avoid rehydration with atmospheric moisture. The δD values are reported relative to standard mean ocean water (SMOW), with analytical error of approximately ±2‰.
Meteoric fluid infiltration in the Argentine Precordillera fold-and-thrust belt | THEMED ISSUE

RESULTS

Mineralogy

Our XRD analysis of oriented samples revealed that each gouge sample contained several mineral phases, and that no size fraction was purely monomineralic. Each of the gouges contained both illite and chlorite as dominant clay phases. The mineralogy of each sample is summarized in Table 2. Qualitative observations of the XRD spectra indicated that the ratio of chlorite to illite decreased greatly in progressively smaller size fractions (Fig. 4A), accompanied by an increase in the amount of smectite in some cases. The presence of at least trace amounts of smectite was ubiquitous, as shown by a peak at 5.2° 2θ in the glycolated state, and this was especially prominent in smaller size fractions.

Nonclay minerals were also present in the several of the size fractions. Quartz appeared in each gouge sample, with the highest relative abundance in course fractions and lowest abundance in fine fractions. Feldspar was present in three of the
Figure 5. York regression plots for the five samples showing the location of the samples in the study area. Plots with yellow backgrounds are fault gouge samples; plot with the blue background is the clay-rich chevron fold sample. Percentage of authigenic 1M$_d$ illite on the x axis is plotted against the measured δD values of size fraction on the y axis. For each sample, the solid black line is the best-fit York regression line, and the dotted lines show the error envelope. Extrapolation to 100% 1M$_d$ illite reveals the δD value of authigenic clay; extrapolation to 0% 1M$_d$ illite reveals the δD value of detrital clay. VSMOW—Vienna standard mean ocean water.
samples, including Tala-F, BQ-G, and SRN-2. Similar to quartz, feldspar was more abundant in the coarse fractions and tended not to be present in the finest fractions. Calcite was a common phase in many of the gouges as well, appearing in many size fractions of the SRN-2 and Tala-F samples.

**Clay Mineral Quantification**

The results of both the MIF and end-member standards matching quantification methods are summarized in Table 3, along with the calculated total proportion of neomineralized (1M<sub>d</sub>) illite and detrital (2M<sub>1</sub>) illite. For each sample, the proportion of 1M<sub>d</sub> illite increased in smaller size fractions as the amount of detrital phases decreased (Fig. 4B). Only one sample (SRN-2) contained a significant amount of smectite, which dominated the smaller size fractions. As a result, this sample resulted in a larger error after York regression analysis.

**Hydrogen Isotopic Composition of Illite and Mineralizing Fluids**

Hydrogen isotopes were measured for five samples totaling 24 size fractions. The δD values are reported relative to SMOW and range from −70‰ to −90‰ ± 2‰ (Table 4). The hydrogen isotopic values of each size fraction represent a composite value that is equal to the total amount of hydrogen contained in all the hydrous phases, including detrital chlorite, detrital illite, authigenic illite, and authigenic smectite, which varied in each size fraction for a single fault. The raw values reported in Table 4 here were used in the York regression to extrapolate the hydrogen isotopic composition of 1M<sub>d</sub> and 2M<sub>1</sub> illite in each sample (Table 5). Along the Jáchal River transect, the Caracol fault (ca. 16–13 Ma) contained authigenic illite with a δD of −91.6‰ ± 5.4‰, the Blanquitos fault (ca. 12–10 Ma) contained authigenic illite with a δD of −86.2‰ ± 2.4‰, and the San Roque fault (ca. 11–2 Ma) contained authigenic illite with a δD of −76.3‰ ± 9.1‰. Further to the south in the Talacasto area, the fault contained authigenic illite with a δD of −82.3‰ ± 5.4‰, while the folded shale showed a δD of −83.2‰ ± 2.0‰.

Using the results from our mixing model, we determined the δD value of fluids in Precordillera thrust fault zones during fault activity and authigenic mineral growth (Table 6). We calculated the δD value of the mineralizing fluid over a temperature range of 100° to 150 °C (Table 6). Results range from the isotopically lightest sample, CW-2 (−59‰ to −85‰), to the heaviest sample, SRN-2 (−40‰ to −73‰).
This sample comes from the western side of the basin sediments were forced out of the sediments due to pore space compaction associated with compression and faulting in the Precordillera thrust belt. Formational fluids were then incorporated along with actively infiltrating meteoric fluids into the fault zone, imparting their δD signatures to the authigenic 1M illite. Because the system involved multiple fluid sources integrated through time scales of millions of years, we do not speculate on specific interpretations of each numerical value. Instead, our interpretation focuses on large-scale temporal trends throughout the time period of Miocene faulting in the Precordillera in order to constrain the processes that drove the changes in δD signatures of meteoric-sourced deformational fluids.

**DISCUSSION**

Our results constrain interpretations of the fluid-mediated processes involved in fault rock generation and geofluid sources. The extrapolation of York regressions and fractionation values gives fluid source δD values—extrapolation to 100% authigenic clay reveals information about the nature of deformational fluid, while extrapolation to 100% detrital clay reveals information about the nature of host rock grains and their associated fluid source(s). The δD signatures of authigenic 1M illite fall within a relatively narrow range (−76.3‰ ± 9.1‰ to −91.6‰ ± 5.4‰), whereas the detrital δD values show two distinct signatures. Three samples, CW-2, Tala-1b, and Tala-F, have detrital δD signatures that range from 61.8‰ ± 17.0‰ to 69.1‰ ± 5.7‰; two samples, BQ-G and SRN-2, have detrital δD signatures that are 88.8‰ ± 9.6‰ and 89.3‰ ± 23.5‰, respectively. Our interpretation for these authigenic and detrital clays is discussed next.

**δD Composition of Authigenic and Detrital Clay Phases**

The oldest fault gouge sample, CW-2 (ca. 16–13 Ma), yields a regression line that shows a distinct trend in δD with grain size (Fig. 5). This sample comes from the western side of the study area, where hanging-wall units are composed primarily of deep-water mudstones. These sediments likely contributed a significant amount of older (Paleozoic) detrital chlorite to the fault zone (von Gosen, 1997). Similarly, the southern Talacasto fault and fold samples (Tala-1b and Tala-F; ca. 12–9 Ma) show a trend that relates the δD values and percentage of detrital material, indicating input of detrital clays from an older source. The 61.8‰−69.1‰ range is consistent with metamorphic chlorite signatures (Taylor, 1974).

The δD values for samples BQ-G (ca. 12–10 Ma) and SRN-2 (ca. 10–2 Ma) do not follow a distinct trend. For these younger two faults, which were sampled in the eastern region of the Jáchal River transect, regression lines are nearly horizontal, reflecting homogeneity of δD values across size fractions within each sample. This uniformity can be interpreted in two ways. First, this could indicate an overall resetting of detrital δD values due to the exchange of hydrogen with the fault fluid during authigenic clay growth. However, it is unlikely that these fault gouge samples reached temperatures well over 150 °C, based on thermochronologic studies of these units (Fosdick et al., 2015). The likely explanation for homogenous δD values is multiple sources of detrital clay minerals, a process we describe in the following paragraph.

For the BQ-G and SRN-2 samples, we propose two distinct detrital mineral sources. The first, metamorphic chlorite, would contribute a portion of hydrogen to the isotopic signature that falls within the range of values for the CW-2, Tala-1b, and Tala-F samples. The second source, modern soil smectite, would also contribute to the hydrogen isotopic signature. Though isotopic studies of soil smectite in this area have not been done, a rough estimation of expected δD composition of smectite using the smectite-water fractionation factor (Capuano, 1992) can be obtained. From the mean annual temperature (16.5 °C), we predict a fractionation of −61.5‰ between smectite and water. Given the average δD of −37.5‰ for modern meteoric fluids calculated from reported δD measurements taken at Mendoza, Argentina, La Serena, Chile, and La Suela, Argentina, the three closest Global Network of Isotopes in Precipitation (GNIP) stations (IAEA/WMO, 2016), we predict that smectite δD values would be around −99‰. Therefore, the presence of significant smectite in these samples would drive the δD values toward the more negative end of the δD spectrum, obscuring the signature of the Paleozoic detrital metamorphic chlorite, as we observe.

**δD Composition of Mineralizing Fluids**

We calculated the approximate fluid δD composition for crystallization temperatures of 125 °C, the median value for our range of possible temperatures. The δD fluid values fall in a range between −57‰ and −72‰ across all five of the samples. The relative homogeneity of fluid isotopic signatures from authigenic clays indicates a common fluid source across the region. The negative δD values of the fluid require significant input from a meteoric source, since no other reservoir has δD values as depleted in heavy isotopes (Fig. 6). Given that authigenic illite δD values are comparable and of meteoric origin, we propose that fluids involved in deformation are surface-sourced fluids, derived in part from the Miocene foreland basin sediments and in part from infiltrating meteoric fluids. Formation fluids in foreland basins may be either shallow marine or meteoric (Taylor, 1974; Sheppard, 1986). In the case of the Argentine Precordillera, stratigraphic studies indicated that the region was not at sea level during deposition (Jordan et al., 2001), so it is likely that formation fluids in the foreland sediments of the Bermejo Basin represent a composite of the Miocene meteoric water that fell both on the basin itself and on the higher-elevation ranges of the Precordillera to the west (Hoke et al., 2014). We surmise that the meteoric-derived formational fluids contained within the basin sediments were forced out of the sediments due to pore space compaction associated with compression and faulting in the Precordillera thrust belt. Formational fluids were then incorporated along with actively infiltrating meteoric fluids into the fault zone, imparting their δD signatures to the authigenic 1M illite. Because the system involved multiple fluid sources integrated through time scales of millions of years, we do not speculate on specific interpretations of each numerical value. Instead, our interpretation focuses on large-scale temporal trends throughout the time period of Miocene faulting in the Precordillera in order to constrain the processes that drove the changes in δD signatures of meteoric-sourced deformational fluids.

**Table 6. δD Fluid Calculations**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>δD illite (%)</th>
<th>Error (%)</th>
<th>δD fluid (100 °C) (%)</th>
<th>δD fluid (125 °C) (%)</th>
<th>δD fluid (150 °C) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW-2</td>
<td>−91.6</td>
<td>5.4</td>
<td>−59</td>
<td>−72</td>
<td>−85</td>
</tr>
<tr>
<td>BQ-G</td>
<td>−86.2</td>
<td>2.4</td>
<td>−57</td>
<td>−67</td>
<td>−76</td>
</tr>
<tr>
<td>SRN-2</td>
<td>−76.3</td>
<td>9.1</td>
<td>−40</td>
<td>−57</td>
<td>−73</td>
</tr>
<tr>
<td>Tala-1b</td>
<td>−83.2</td>
<td>2.0</td>
<td>−54</td>
<td>−64</td>
<td>−73</td>
</tr>
<tr>
<td>Tala-F</td>
<td>−82.3</td>
<td>5.4</td>
<td>−50</td>
<td>−63</td>
<td>−75</td>
</tr>
</tbody>
</table>

**Figure 6. δD scale showing the composition of surface-sourced (solid gray bars) and deeply sourced, metamorphic fluid reservoirs (dashed gray bar; Sheppard, 1986) compared to the deformation fluid signatures measured in this study (heavy black bar). For reference, the average δD composition of meteoric fluid in the study area and ocean water (SMOW) are both plotted as gray bars. VSMOW—Vienna standard mean ocean water.**
Drivers of Change: Climate or Tectonics

Despite the differences in hanging-wall rock composition and location in the study area, all fault and fold samples point to meteoric-derived, surface-sourced fluids. Since the isotopic composition of meteoric waters can be modified by both climatic and tectonic processes, the $\delta D$ values preserved in fault gouge clays and, more specifically, the trends observed through time in these $\delta D$ values will reflect the influence of these processes. There are two possible scenarios for major drivers of change in the isotopic composition of meteoric-derived deformational fluids and associated neoformed clay minerals: (1) the gradual uplift of the drainage area due to tectonic shortening of the Precordillera fold-and-thrust belt, and (2) the cooling and aridification of climate during the Miocene in this region of South America. The fractionation of stable hydrogen (and oxygen) isotopes in atmospheric H$_2$O by these processes would have opposite and competing effects on the composition of meteoric fluids.

For scenario 1 (uplift), the Rayleigh distillation of rainwater as it moves up in elevation causes progressively higher-elevation sites to receive more negative isotopic precipitation (Gat, 1996). The late Miocene in central South America was associated with the progressive uplift of the Precordillera fold-and-thrust belt and subsequent uplift of the Sierras Pampeanas (Sobel and Streeker, 2003; Hoke et al., 2014). The surface uplift of these ranges, therefore, would be associated with progressive evolution of meteoric water toward more negative stable isotopic values through time. In scenario 2 (climate), there would be the opposite effect. The late Miocene was a time of general cooling and aridification in the region of the Precordillera (Flower and Kennett, 1994; Cerling et al., 1997). Cooling of the climate was associated with the growth of the Antarctic ice sheet, which sequestered negative hydrogen isotopes in the ice sheet and progressively enriched the oceanic reservoirs in heavy isotopes (Zachos et al., 2001). This would make precipitation sourced from the oceans become less negative through time. Alternatively and/or additionally, the trend toward heavy isotopic enrichment with time may have been a result of aridification, where basinal waters become evaporatively enriched in heavy isotopes in arid climates (Sheppard, 1986). Studies have shown that the late Miocene in the south Central Andes may have experienced such climatic aridification (Flower and Kennett, 1994; Cerling et al., 1997; Jordan et al., 2001). Regardless, both of these scenarios offer a trend driven by changing climate patterns that caused a shift in the stable isotopic values from more negative (light) toward less negative (heavy) values. Because these scenarios have opposite effects on the composition of stable isotopes in meteoric and, therefore, deformational fluids, our data set can distinguish between these two competing processes of isotopic fractionation.

To test the two scenarios, we plotted the $\delta D_{ave}$ values for each fault sample along with published estimates of fault activity (Fig. 7), where ages are from Jordan et al. (2001), Allmendinger and Judge (2014), and Levin et al. (2014). This plot reveals that progressively younger faults from the Jáchal River transect have meteoric fluid signatures that have progressively heavier $\delta D$ signatures. This general trend in the $\delta D$ value of meteoric fault fluids, being less negative through time, is consistent with a climate-dominated signal, as described in scenario 2. Notably, we do not observe a decrease in the $\delta D$ values as predicted by scenario 1, indicating that any topographic-related (uplift) isotopic signal is insignificant. We note that the combined effect of these two scenarios would have a dampening effect on the intensity of the changes observed in our isotopic $\delta D$ values, such that the climate signal dominating the fault fluid signature may be even more subdued than full isotopic trends in Miocene precipitation.

Other stable isotopic studies in the Central Andes have revealed similar patterns of isotopic enrichment. Kleinert and Streeker (2001) observed a progressive increase in $\delta^{18}O$ and $\delta^{13}C$ of paleosol from 12 Ma to present, attributing the trend to increased aridity and evaporation in the Santa Maria Basin of the Northern Sierras Pampeanas (northeast of our study area), interpreted in part to be a consequence of uplifting mountain ranges and developing rain-shadow effects during the middle Miocene. Similarly, Latorre et al. (1997) analyzed paleosol carbonates from a stratigraphic section close to those of Kleinert and Streeker (2001) and observed a positive shift in $\delta^{18}O$ starting around 9 Ma, which they too attributed to changing climatic patterns and increased aridity. A more recent study of paleosol carbonate stable isotopes similarly documented increasing $\delta^{18}O$ values since ca. 7.14 Ma, corresponding to an ash bed near the bottom of the studied stratigraphic section (Hynek et al., 2012).

Today’s meteoric fluid composition in the Precordillera is monitored by nearby sites in the GNIP. Three of the closest monitoring sites, Mendoza, Argentina, La Serena, Chile, and La Suela, Argentina (Fig. 2), show an average meteoric $\delta^{18}O$ fluid of $-37.5\%$ ($n = 130$), with 50% of $\delta D$ measurements falling within the range of $-23\%$ to $-49\%$ (Fig. 7; IAEA/WMO, 2016). These three monitoring locations at relatively low-altitude sites may be biased toward heavy...
isotopes relative to the Central Andes region as a whole. However, recent studies of stable isotopes in precipitation and river waters around Mendoza, Argentina, confirm that the stable isotopic composition of surface waters correlates with the average elevation of the drainage area (Hoke et al., 2009, 2013). Our measured values of δD in progressively younger faults follow the trend of increasing heavy hydrogen of Miocene meteoric waters (72% to 58%), as preserved in clays of the Precordilleran, providing evidence for a dominant climatic driver on evolving δD signatures of geofluids in this part of the Central Andean fold-and-thrust belt.

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