Ordovician K-bentonites in the Argentine Precordillera: relations to Gondwana margin evolution

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Abstract: Ordovician K-bentonites have now been recorded from >20 localities in the vicinity of the Argentine Precordillera. Most occur in the eastern thrust belts, in the San Juan Limestone and the overlying the Gualcamayo Formation, but a few ash beds are known also from the central thrust belts. The oldest occur in the middle Arenig *I. victoriae lunatus* graptolite (*Oe. evae* conodont) Zone, and the youngest in the middle Llanvirn *P. elegans* (*P. suecicus*) Zone. Mineralogical characteristics, typical of other Ordovician K-bentonites, include a matrix of illite/smectite mixed-layer clay and a typical felsic volcanic phenocryst assemblage: biotite, beta-form quartz, alkali and plagioclase feldspar, apatite, and zircon, with lesser amounts of hornblende, clinopyroxene, titanite and Fe–Ti oxides. The proportions of the mineral phases and variations in their crystal chemistry are commonly unique to individual (or small groups of) K-bentonite beds. Glass melt inclusions preserved in quartz are rhyolitic in composition. The sequence is unique in its abundance of K-bentonite beds, but a close association between the Precordillera and other Ordovician sedimentary basins cannot be established. The ash distribution is most consistent with palaeogeographical reconstructions in which early Ordovician drifting of the Precordillera occurred in proximity to one or more volcanic arcs, and with eventual collision along the Andean margin of Gondwana during the mid-Ordovician Ocloyic event of the Famatinian orogeny. The Puna–Famatina terrane northeast of the Precordillera might have served as the source of the K-bentonite ashes, possibly in concert with active arc magmatism on the Gondwana plate itself.

Lower Palaeozoic K-bentonites (altered volcanic ashes) are widely distributed on the continents bordering the former Iapetus Ocean, especially in northwestern Europe and eastern North America. Local and regional studies during the last decade have added a wealth of new information about their geographical and stratigraphical distribution, geochemistry, and mineralogy as well as their tectono-magmatic and palaeogeographical significance (Kolata *et al.* 1996; Bergström *et al.* 1997; Huff *et al.* 1998). In South America, K-bentonites are as yet unknown in the Cambrian and Silurian and were discovered in the Ordovician only a few years ago (Huff *et al.* 1995*a*). During the past few years, many Lower and Middle Ordovician K-bentonite beds have been found in the Precordillera of western Argentina; indeed, this region has some of the most abundant ash beds known from that period anywhere in the world.

K-bentonite geochemistry may provide highly significant information about the tectono-magmatic nature of the source area, and the distribution patterns of individual ash beds or complexes of such beds may shed additional light on the former positions of continental plates. Specific chemical and mineralogical features of primary phenocrysts can serve as important criteria for regional stratigraphical correlation of beds and bed sequences, whether expressed as elemental ratios of individual grains or in the immobile element chemistry of bulk K-bentonite samples (Kolata *et al.* 1987; Huff *et al.* 1992; Bergström *et al.* 1995). K-bentonite beds also provide important evidence regarding the timing and location of orogenic events because they typically originate from source volcanoes situated at or near tectonically active plate margins (Kolata *et al.*

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1987; Huff *et al.* 1992; Bergström *et al.* 1995). Further, dating of K-bentonite beds or complexes of beds provides precise age dates on periods of volcanism associated with continental margin subduction events. Therefore, when trying to unravel the pre-Andean evolution of the western Gondwana margin it is appropriate to consider the various types of evidence provided by the K-bentonites. The first step in any such evaluation is to explore the vertical and horizontal distribution of these ashes, both locally and regionally, and to clarify their age and distribution patterns. Without establishing the position of these beds in a reliable biostratigraphical framework, no meaningful regional comparisons can be made, and the assessment of their palaeogeographical significance is seriously hampered. In view of this, the first part of the present contribution will assess the stratigraphical and geographical distribution of the Ordovician K-bentonites in the Argentine Precordillera. We will also make a comparison with the geographical and stratigraphical distribution of Ordovician K-bentonite complexes in North America (Laurentia) to examine whether or not they are likely to represent the same ash falls. If they do, it would obviously suggest rather close proximity of Laurentia to the Precordillera during the time of the ash fall (Dalziel 1997). The absence of correlative beds on these two land masses would be consistent with models which argue for a wide Iapetus at the time of eruption (Astini *et al.* 1995; Thomas & Astini 1996), unless prevailing wind direction severely skewed ash distribution. Thus, K-bentonites may serve as a means of testing palaeogeographical reconstructions and models of the Iapetus Ocean.

A second part of the present contribution deals with the mineralogy and geochemistry of Precordilleran K-bentonites and their tectonomagmatic significance. We show that melt inclusion composition and the whole rock ratios of immobile elements provide evidence for collision-margin volcanism. A final part summarises the evidence at hand bearing on the evolution of the Gondwana margin, and the Ordovician geological history of the Precordillera. Our investigations of the Argentine Ordovician K-bentonites are continuing and some of the data presented below are of a somewhat preliminary nature.

Occurrence

Since their discovery in the Precordillera in 1994, Ordovician K-bentonites have been recorded from more than 20 localities in a region extending about 250 km in a north–south direction across parts of San Juan and La Rioja Provinces. Some of the principal localities are shown in Fig. 1. No ash beds have been observed in the Ordovician outcrops in the San Rafael region some 200 km south of Mendoza. Likewise, as noted by Bergström *et al.* (1996), no K-bentonite beds are known from the locally rather strongly tectonized slope and basin successions in the western Precordillera, such as the well-exposed Middle Ordovician sequences near the northern end of Sierra de la Invernada about 40 km northeast of Talacasto (Fig. 1), or in the outcrops along the mountain front from Calingasta northwards to the Jáchal River. Most of the known K-bentonites occur in the eastern thrusts of the thrust-and-fold belt, where they are quite common in the upper section of the San Juan Limestone, characterized by massive platform carbonates with an early Palaeozoic Laurentian fauna, and in the overlying deep water graptolitic shales of the Gualcamayo Formation. A few ash beds are also known from the central thrusts. For convenience, we will briefly review the geographical and stratigraphical distribution patterns in terms of three main distribution areas, namely the Guandacol region in the northernmost Precordillera, the Jáchal region some 100 km to the south, and the San Juan region about 150 km still farther to the south (Fig. 1). Only a few key sections are discussed here; for further information, see Bergström *et al.* (1996).

The oldest recorded Palaeozoic K-bentonites in the Precordillera occur in the middle Arenig *Oe. evae* Zone (Hünicken & Sarmiento 1982, 1985) in the topmost part of the Lower Ordovician San Juan Limestone in outcrops along the Gualcamayo River in the Guandacol region. In the overlying, about 200 m thick, Gualcamayo Formation, which ranges from the Upper Arenig to at least the Middle and probably Upper Llanvirn, there are numerous ash beds, especially along a small tributary to the Guandacol River (26°45′34″S, 68°39′12″W) where more than 170 separate ash beds have been observed. This is by far the most extensive suite of Ordovician K-bentonites recorded from an outcrop anywhere in the world and ranks slightly above the Lower Silurian K-bentonite succession at Dob's Linn in Scotland which contains 135 beds (Merriman & Roberts 1990). Most (*c.* 85) of the ash beds, which range in thickness from less than 1 mm to more than 50 cm, occur in the upper Arenig *U. austrodentatus* Zone (Brussa & Astini 1997) but many beds are present also in slightly older and slightly younger strata. Excellent sections of coeval strata, but with fewer K-bentonite beds, are present at the Quebrada de Los Saltitos and

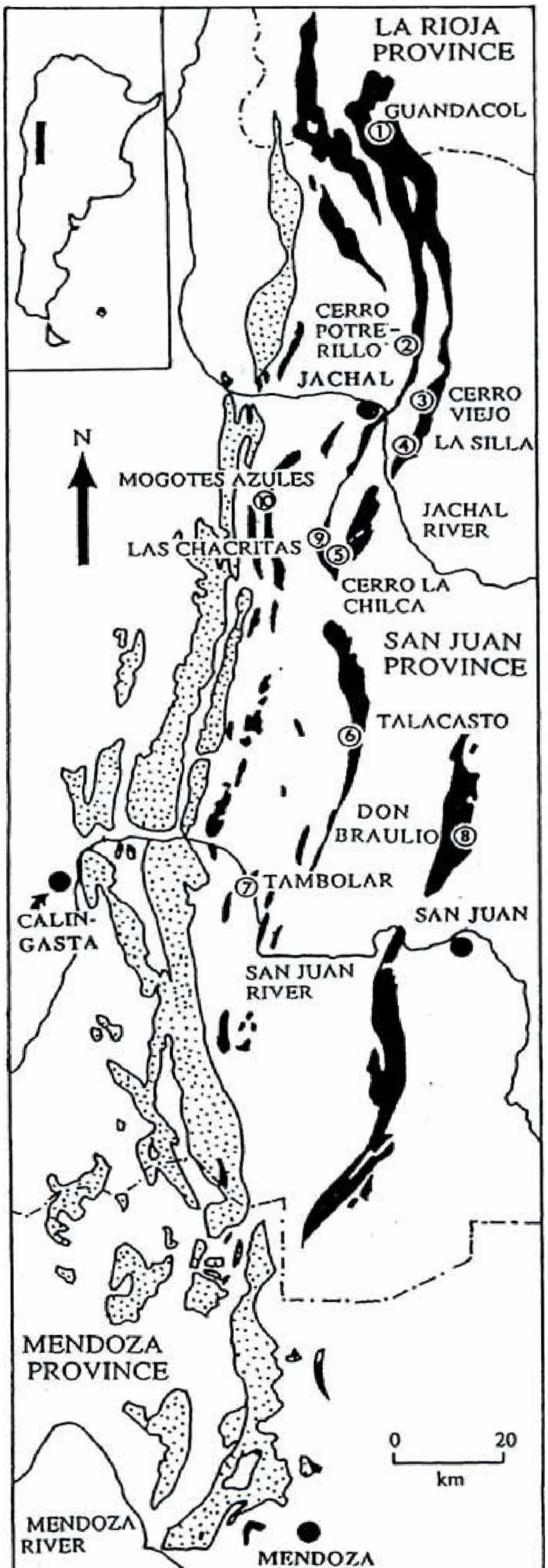

Fig. 1. Location map of the Precordillera, Argentina, showing some of the principal localities where K-bentonites are exposed. The inset map of Argentina shows the position of the Precordillera. The areas in black are the Ordovician outcrop areas of the eastern and central thrust belts, and the stippled areas represent the Ordovician outcrop areas of the western thrust belts. Numbered locations refer to the principal sections used in this study.

in the Quebrada Nazareno, a short tributary branch between Quebrada Las Plantas and Quebrada de Potrerillos in the Guandacol area (Fig. 1).

In the Jáchal area, there are about 30 individual K-bentonite beds in the Los Azules Formation (equivalent to the Gualcamayo Formation elsewhere) at Cerro Viejo (Huff *et al.* 1995*a*; Bergström *et al.* 1996; Cingolani *et al.* 1997) and up to a dozen such beds have also been recorded from the upper part of the underlying San Juan Limestone. A concordant U–Pb zircon age from Cerro Viejo was reported by Huff *et al.* (1997*b*) as 464 ± 2 Ma which they considered to be the age of the base of the *U. austrodentatus* Zone. Beds of the latter complex, which post-date the oldest K-bentonite beds in the Guandacol region, are well exposed at many localities, such as Cerro Potrerillo, Cerro La Chilca, and La Silla (Fig. 1), and also in the still poorly dated successions at Las Chacritas (30°33′51″S, 68°51′53″W) (Albanesi & Astini 1994; Astini 1994) and Mogotes Azules (30°21′15″S, 68°55′02″W). Multiple K-bentonite sequences are present at all of these localities but none are as extensive as the middle Arenig K-bentonite complex in the Guandacol region.

The most accessible K-bentonite locality in the San Juan region is in a highway road cut at Quebrada de Talacasto about 55 km north-northwest of San Juan. As described by Bergström *et al.* (1996) there are 30 individual ash beds, the thickest ones 10–15 cm, within a 110 m thick succession of the upper San Juan Limestone. At least the upper portion of this complex is probably comparable with the K-bentonite complex in the Gualcamayo Formation at Cerro Viejo. The considerable thickness of some beds at the latter locality may be due to the fact that the section is more condensed and some of the thick beds may be composed of several, in time relatively closely spaced, ash falls that are represented by separate ash beds in the thick Talacasto succession. A single bed about 50 m below the top of the San Juan Limestone at the Tambolar section in the San Juan River valley (Lehnert 1995; Bergström *et al.* 1996) is one of the oldest K-bentonite beds known from the Precordillera.

In terms of stratigraphical distribution, the oldest K-bentonites currently known in the Precordillera are of middle Arenig age and the youngest are of middle to upper Llanvirn age (Bergström *et al.* 1996). No ash beds have been observed in younger parts of Middle Ordovician or Upper Ordovician strata. Figure 2 is a north–south transect showing the main patterns of K-bentonite bed distribution. The high concentration of ash beds in the upper Arenig–lower Llanvirn in the Guandacol region may suggest the general direction toward the location of the

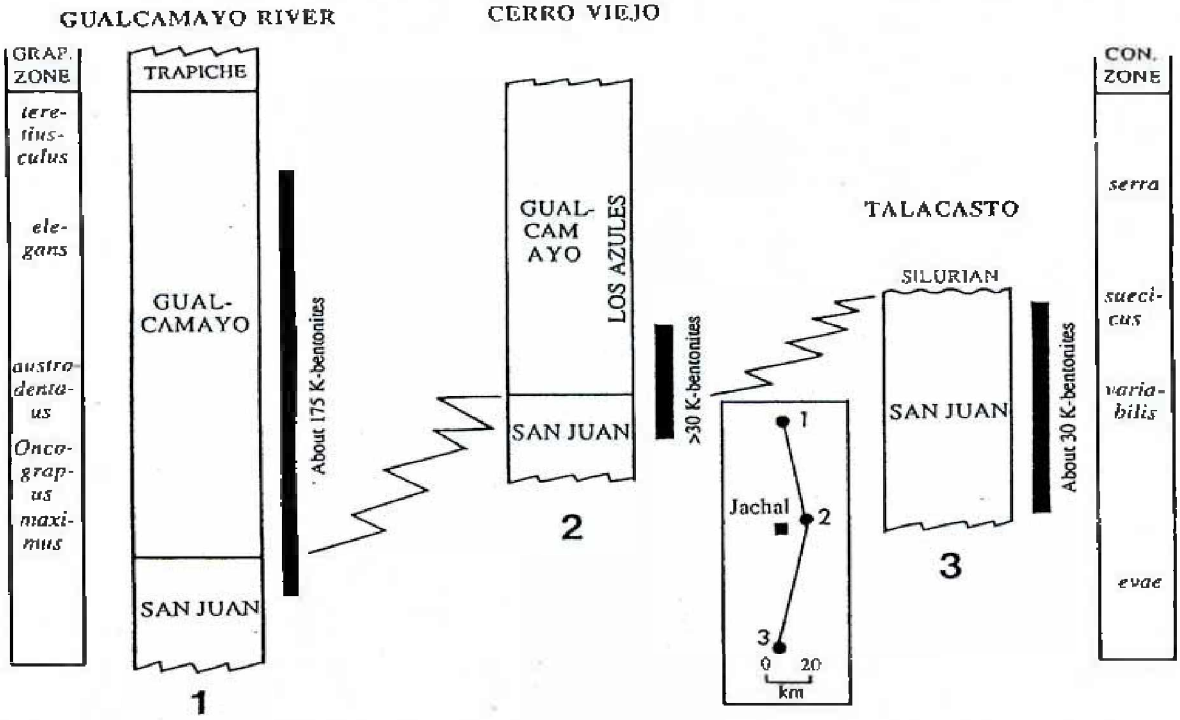

Fig. 2. A north–south transect from Guandacol to Talacasto showing the stratigraphic position of the K-bentonite sequences. The north to south transgressive nature of the graptolitic shales of the Gualcamayo Formation (Astini *et al.* 1995) is well documented by the change in facies containing the K-bentonite beds. The column on the right lists the applicable conodont zones.

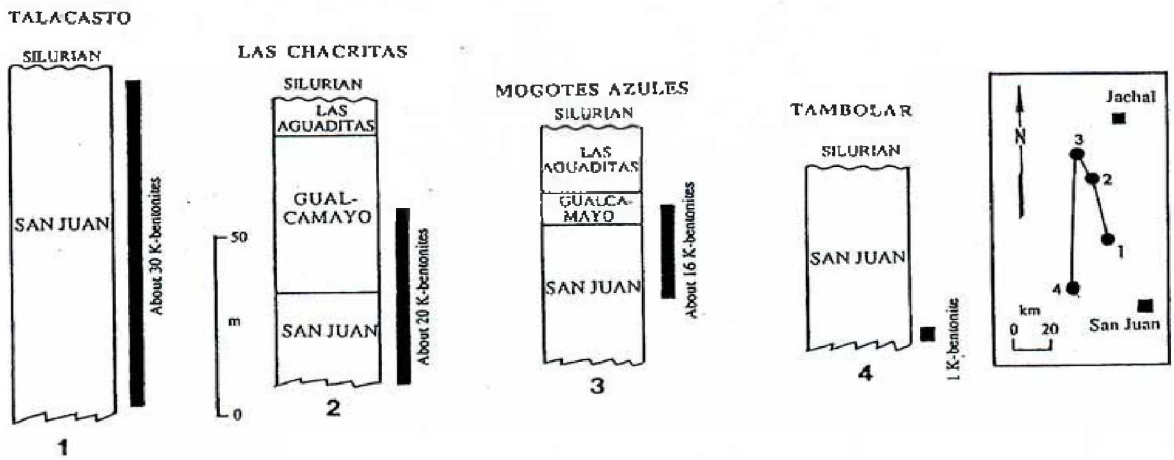

Fig. 3. A transect through the eastern and central thrust belts showing the stratigraphic position of the K-bentonite sequence. There is no obvious thinning of beds from one region to the other, but there is a noticeable increase in the number of preserved beds toward the north and east.

source area; alternatively, it may reflect the fact that these ash beds are in deeper-water dark shales that represented an environment which was more favourable for preservation of volcanic ashes than the shallower-water carbonate dominated depositional environments of the San Juan Limestone in the Jáchal–San Juan regions.

In terms of east–west geographical distribution, there is an obvious trend from many beds in the eastern thrust belts to relatively few in the central thrust belts (Fig. 3). In many sections in the central belts, the upper San Juan Limestone and the overlying Gualcamayo Formation are not preserved, being cut out by an unconformity (Astini *et al.* 1995; Lehnert 1995*b*). Hence, in those sections the K-bentonite rich interval of the eastern belt may not be represented. Elsewhere, Silurian strata overlie younger Ordovician units, even in the central ranges (Astini & Maretto 1996)

Ordovician volcanism

The widespread occurrence of K-bentonite beds in the Argentine Precordillera constitutes one of the most extensive suites of such beds known anywhere in the Ordovician System of the world and serves as testimony to the high intensity of explosive volcanism along this margin of Gondwana during the early and middle parts of that period. Previous and ongoing studies of the sedimentology, mineralogy and geochemistry of these beds provide both insight and constraints concerning the magmatic, tectonic and paleogeographical settings under which the explosive volcanism was generated, and also permit comparisons with lower Palaeozoic K-bentonites on other continents. While our most recent field work has revealed an extensive succession of K-bentonite beds in the exposures along the Gualcamayo River and its tributaries in western La Rioja Province, most of our detailed particle-size, mineralogical, and geochemical studies to date have been on samples from the extensive sections at Cerro Viejo, near Jáchal, and at Talacasto, north of San Juan, in San Juan Province (Fig. 1). Further, while most known evidence for pre-Andean explosive volcanism on the Gondwana margin is preserved in the Ordovician sections of the Argentine Precordillera, additional beds of pyroclastic origin have also been reported from the Balcarce Formation of the Tandilia region, south of Buenos Aires (Dristas & Frisicale 1987). This formation is considered to be Ordovician in age based on *Cruziana* ichnofaunal evidence and a K–Ar radiometric age of 396 ± 11 Ma from a cross-cutting dyke (Cingolani *et al.* 1985). At least one, and perhaps as many as four, altered pyroclastic beds occur in the white quartzite sequence which ranges from 18 to 500 m in thickness and unconformably overlies Precambrian basement (Dalla Salda *et al.* 1988). In contrast to the illite/smectite-rich beds of the Precordillera, the Balcarce beds consist mainly of well crystallized kaolinite, indicated by sharp X-ray powder diffraction reflections at 7.12 Å and 3.58 Å, with occasional crystals of altered ilmenite, and are considered to be the product of altered mafic ashes (Dristas & Frisicale 1987). They may legitimately be called tonsteins because of their clay mineralogy and apparent pyroclastic origin, although, in contrast to most tonsteins, they occur in quartzites and have no association with coal measures. Their relationship to the Precordillera K-bentonites, if any, is unclear, other than that they also appear to represent evidence of fallout ash accumulation sometime during the Ordovician. The Balcarce beds most probably represent an entirely different tectonic setting from that of the felsic Precordillera beds, which will be the focus of the remaining discussion.

K-bentonite mineralogy

Precordillera K-bentonites consist principally of authigenic clay minerals, carbonates, sulphates, oxides, and sulphides, plus primary magmatic quartz, titanite, apatite, biotite, feldspar, pyroxene, amphibole, zircon and Fe–Ti oxides (Huff *et al.* 1995*a*; Krekeler *et al.* 1995; Cingolani *et al.* 1997; Prokopenko *et al.* 1997). The clays and other secondary minerals provide information about the alteration processes that have affected the fallout ash, and the primary pyroclastic crystals (herein called phenocrysts) retain information concerning composition and origin of the parental magma as well as the timing and tectonic setting of the source volcanism. The primary mineral suite is characteristic of the felsic calc-alkaline nature of the tephras from which these, as well as the majority of Lower Palaeozoic K-bentonites, are derived.

Clay mineralogy

The clay mineral fraction of Precordilleran K-bentonites consists of R1 to R3 ordered mixed-layer illite/smectite (I/S) with the illite content ranging from 72 to 95% (Fig. 4). The X-ray diffraction (XRD) traces shown in Fig. 4 are representative of more than 50 such analyses of oriented, glycol-saturated, $<2\,\mu m$ size fractions of clay samples from Talacasto, Cerro Viejo,

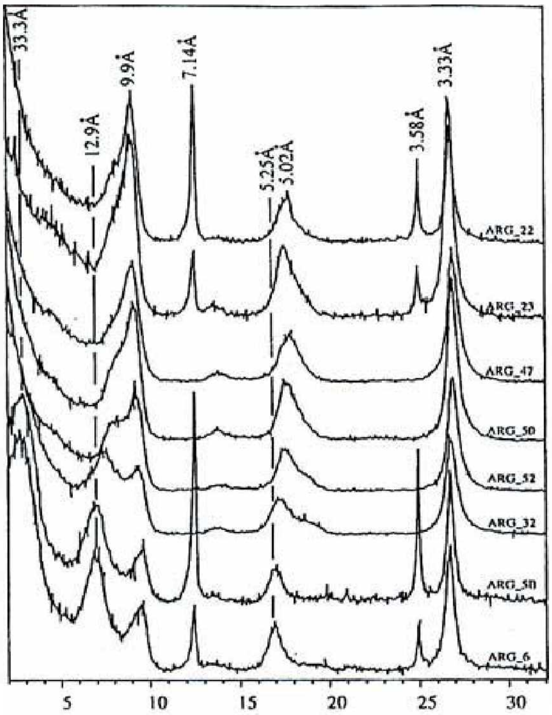

Fig. 4. Powder X-ray diffraction patterns of oriented, glycol-saturated slides of the <2 μm fraction of eight representative Precordillera K-bentonites. All contain illite/smectite as the principal clay mineral and are arranged in sequence from R1 ordered I/S with 72% I at the base to R3 ordered I/S with 95% I at the top as indicated by peaks between 9.9–12.9 Å. Low-angle reflections at 33.3 Å indicate R1 ordering. Percentages were calculated using NEWMOD (Reynolds 1985). Samples 5B & 6 are from Cerro Viejo, 32 is from La Silla, 47, 50 & 52 are from Talacasto, and 22 & 23 are from Quebrada Las Plantas at Guandacol. Kaolinite is a major constituent in several samples and can be identified by peaks at 7.14 Å and 3.58 Å.

Guandacol, and La Silla. The relative proportions of illite and smectite as well as the nature of their ordered interstratification were determined using the computer program NEWMOD© (Reynolds 1985). The traces in Fig. 4 are stacked to show the range of illite found. With few exceptions, I/S is the dominant clay mineral component of Lower Palaeozoic K-bentonites throughout the world, and reflects both the vitric-rich nature of the original tephra and also their calc-alkaline character. The relative proportions of illite and smectite layers are a function of several factors, including thermal history, extent of K-metasomatism, availability of potassium and aluminium in the system, and initial composition of the glass alteration products, generally considered to have been smectite. Kaolinite is also present in some K-bentonites, at times in nearly equal proportion to the I/S. However, kaolinite is less common in Ordovician K-bentonites than in Silurian K-bentonites, in which it is common and, even occasionally, the dominant clay mineral (Teale & Spears 1986; Huff *et al.* 1997*c*). In the Precordillera, Lehnert & Keller (1994) have recorded very low-grade metamorphic temperatures based on conodont alteration index (CAI) studies in the central and western zones. Most K-bentonites in the eastern thrust belts, however, were not subjected to temperatures greater than about 100°C (Lehnert & Keller 1994; Ortega *et al.* 1996).

Phenocryst mineralogy

Figure 5 shows examples of primary volcanogenic phenocrysts from bed ARG-3 at Cerro Viejo, which are typical of many Precordilleran K-bentonites. Quartz is very common and frequently occurs in beta-form morphology, characteristic of volcanogenic quartz (Bohor & Triplehorn 1993). Individual crystals average 0.2 mm in diameter, based on optical measurements of over 400 grains from four separate K-bentonite beds at Cerro Viejo (Fig. 6). Previous studies (Huff *et al.* 1996) of K-bentonite phenocrysts report that despite the loss of original pumice and glass particles during diagenesis, some phenocrysts remain unaffected and can serve as reliable proxies for original grain size. Thus, it may be possible to speculate on some dynamic aspects of ash emplacement, such as the eruptive mechanism, by comparing grain-size measurements with published theoretical models of eruptive plume dispersion. Quartz was selected for size measurement because of its relatively equidimensional character and thus the greater likelihood that its average diameter would more closely reflect transport conditions for ideal spherical grains (Walker 1981). The exponential decrease in grain size of fallout tephra as a function of distance from the source is well known (Carey *et al.* 1989; Sigurdsson & Carey 1989) and holds equally well for co-ignimbrite and plinian plumes. A comparison of the Cerro Viejo grain-size data with theoretical models suggests that particles averaging 0.2 mm in diameter were transported at least 200 km from the source vent or caldera. This assumes, for example, a minimum plume height of 35 km and a sustained wind velocity of 50 km/hr, both of which are well within the range of recent large-scale explosive eruptions. The absence of coeval volcanism anywhere on the Precordillera further suggests the source volcanoes were not in the immediate

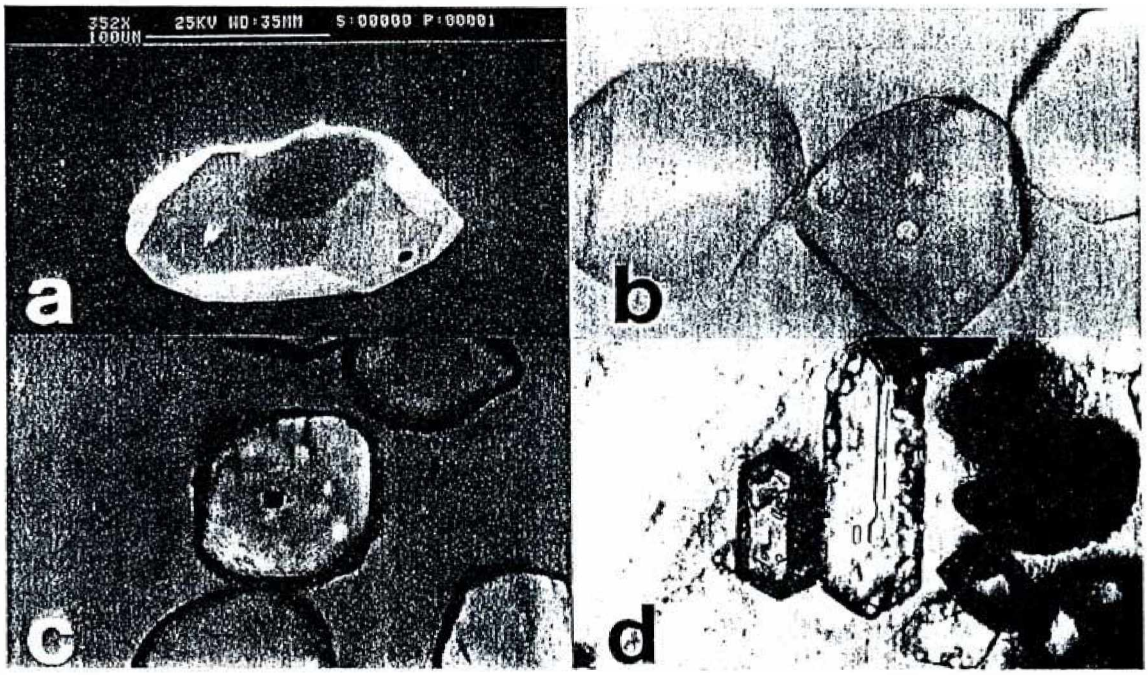

Fig. 5. Examples of volcanogenic phenocrysts from bed ARG-3 at Cerro Viejo. (a) SEM photograph of a zircon crystal. The scale bar is 100 μm. (b) Beta-form quartz crystals averaging 0.2 mm in diameter. Note the clear, round glass melt inclusion in the centre crystal. (c) Beta-form quartz crystal with a sphene inclusion. (d) A zircon (shorter) and apatite (longer) crystal, both containing elongated melt inclusions. Note internal zoning in the zircon.

vicinity. A likely source is the Puna–Famatina terrane to the north (Bahlburg & Hervé 1997) which appears to have had a geodynamic history similar in age and style to the Precordillera.

Some quartz crystals contain pristine glass melt inclusions, which are clear, rounded or ovoid in shape, and range between 20 and 75 μm in diameter. We report below the results of microprobe analyses of some melt inclusions which serve to constrain the composition of the pre-eruption parental magma. Some grains also contain inclusions of titanite and opaque minerals. Zircon and apatite are both common constituents of Precordillera K-bentonites. Zircon crystals are euhedral and typically 100–200 μm in length, with high aspect ratios. Some show internal zoning and also contain elongated melt inclusions (Fig. 5). Apatite grains tend to be somewhat larger than zircons and also contain melt inclusions.

Pyroxene was identified in at least five K-bentonite beds at Talacasto where they constitute as much as 80% of the non-opaque heavy mineral fraction (Prokopenko *et al.* 1997). The crystals appear as angular, highly fragmented grains ranging from pale green to greenish-brown in colour under the petrographical microscope. Microprobe analyses (Fig. 7) show that they are calcium-rich clinopyroxenes with a diopside composition. Their occurrence is somewhat unusual when compared to the North American and Baltoscandic K-bentonites which do not have them, but it is consistent with the general mineralogy of volcanic rocks generated in silicic magma chambers. For example, Hildreth (1979) reported both orthopyroxenes and clinopyroxenes from the Bishop Tuff, a layered silicic ash-flow tuff.

The directions of compositional trends of clinopyroxenes from the Talacasto section present some systematic changes that appear to vary with stratigraphical position. For example, augites with the least Ca-enrichment from the two lowest beds in the section (Fig. 7) display a tholeiitic differentiation trend (Sack & Ghiurso 1994) whereas crystals from the uppermost parts of the section are much more clustered and show little compositional variation, or show trends along the Ca–Fe line of the clinopyroxene quadrilateral. Clinopyroxenes crystallizing from felsic magmas would be expected to show enrichment in Fe and Ca if mixing with more mafic magmas

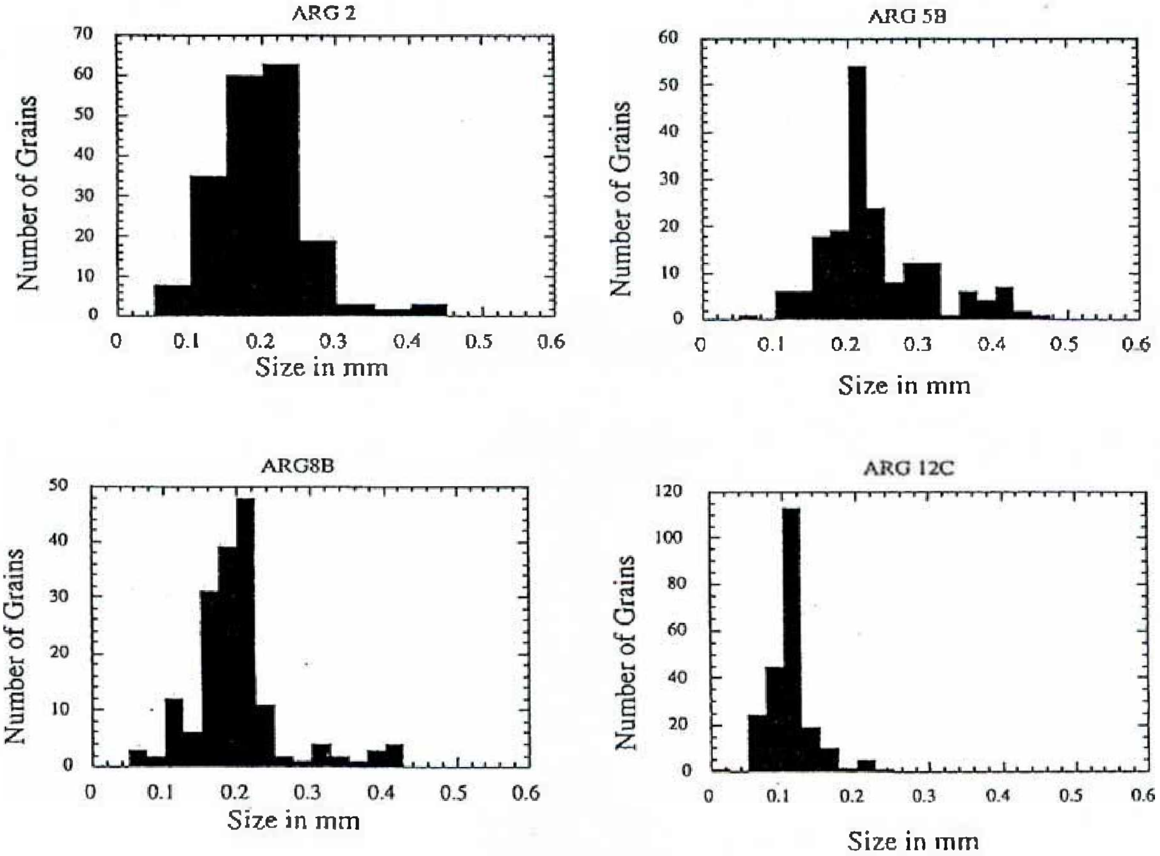

Fig. 6. Histograms of optical measurements of the maximum diameter of quartz grains from four K-bentonite beds at Cerro Viejo. For all beds the distribution is unimodal with mean diameters of 0.2 mm.

were involved. Other variables, such as changes in oxygen fugacity, which will affect the amount of Fe in the clinopyroxene structure, and assimilation of continental crustal rocks, which might be expected to dilute the Ca–Fe content, might also influence the observed variations. Beds in the upper part of the section contain both high-Ca and low-Ca clinopyroxenes which may reflect coexisting crystallization of both phases. Thus, pyroxene compositions in the Talacasto section suggest a somewhat more complex history of magmatic development than previously shown by other Ordovician K-bentonites in the Precordillera or elsewhere along the Iapetus margin. Such information should ultimately prove quite valuable in interpreting the tectonic history of this region of the Gondwana margin.

Feldspars constitute one of the more common phenocryst phases in Precordilleran K-bentonites, in part because they occur as both primary and authigenic minerals. Feldspars normally make up to as much as 20% of the total grain population and range from 0.2 mm, for the majority of grains, occasionally up to 0.5 mm. The larger grains appear to be mainly authigenic albite, however, while the smaller grains are characteristically primary plagioclase and K-feldspar. Preliminary microprobe studies of the feldspar population of several beds at Cerro Viejo (Krekeler *et al.* 1995) revealed a broad range of compositions. In particular, two K-bentonites, ARG9 and ARG10, have anomalously high percentages of volcanogenic feldspar, constituting nearly 40% of the total grain population. Microprobe analyses indicate that the plagioclase compositions differ from bed to bed and range in composition from An_{31} to An_{80}. Sanidine compositions were obtained from a single K-bentonite, ARG12, where they range from Or_{26} to Or_{19}. A ternary diagram of all feldspar data, including authigenic grains, is presented in Fig. 8. This range of feldspar compositions provides additional evidence of the heterogeneous nature of the source magmas.

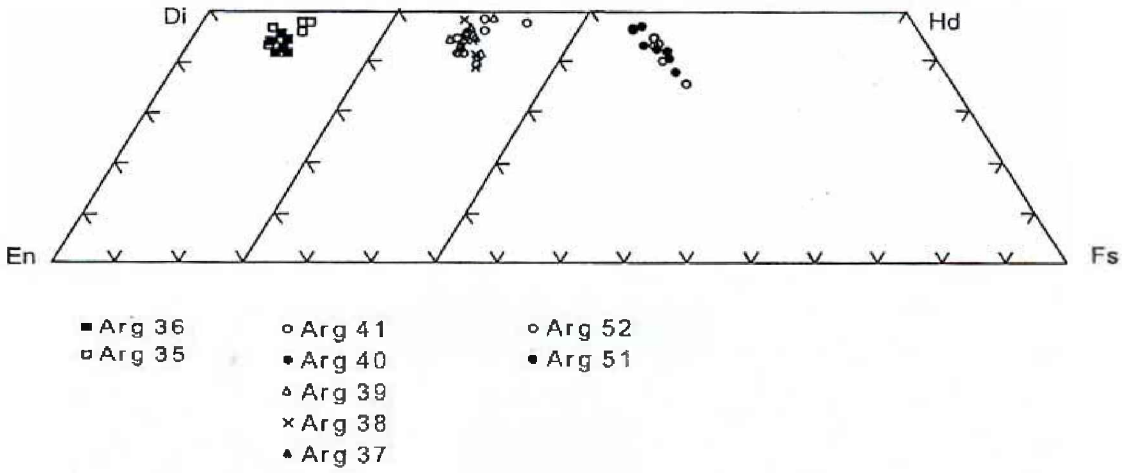

Fig. 7. Compositional plot of clinopyroxenes from the Talacasto section shown on the diopside (Di)–hedenbergite (Hd)–enstatite (En)–ferrosilite (Fs) quadrilateral. Most have compositions near the diopside end of the diopside-hedenbergite series. Sample numbers are arranged in stratigraphic order with Arg-35 at the top of the section and Arg-52 at the bottom.

Fe-oxides occur commonly in the K-bentonites and have been identified using reflected light microscopy and X-ray powder diffraction. Petrography reveals that some Fe-oxides have nucleated on other opaque phases such as ilmenite and magnetite and were most probably derived from them by alteration. The Fe-oxides occur in a variety of crystal habits including tetragonal bipyramids, isometric cubes, and rounded radiating grains. Many rounded grains have crystal faces developed on the surface: X-ray diffraction shows them to be dominantly goethite.

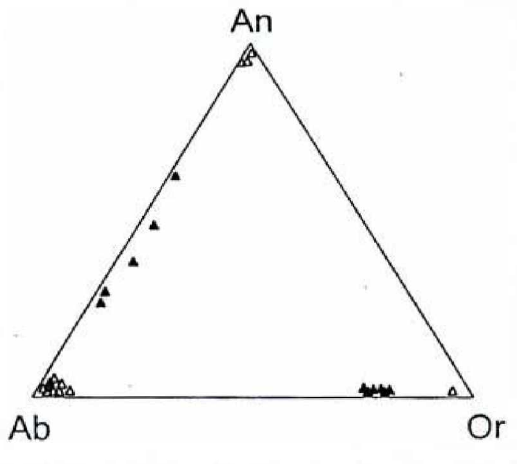

Fig. 8. Composition of both magmatic and authigenic feldspars from Cerro Viejo shown on the albite (Ab)–anorthite (An)–orthoclase (Or) ternary diagram. Pure end-member specimens are considered to be authigenic. Primary magmatic sanidine ranges from Or_{26} to Or_{19} in composition, and plagioclase varies between An_{31} and An_{80}.

Geochemistry

Magmatic and tectonic discrimination diagrams can be used to infer original magma composition and source volcano settings relative to plate margins. Microprobe analysis of glass melt inclusions in quartz grains from Cerro Viejo (Table 1) yielded oxide totals near 96.6%, and the data were plotted on a total alkalis versus silica (TAS) diagram (Fig. 9). Care was taken to minimize Na-loss by reducing the beam current, enlarging the spot size, and averaging repeated analyses (Spray & Rae 1995; Hanson *et al.* 1996) so it is considered that most of the remaining 3.4% consists of H_2O. This conclusion is supported by previous studies of glass melt inclusions in which total O was measured and the major deficit in the oxide total was found to be H_2O (Nash 1992). Silicic magmas may also contain some exsolved volatile constituents which would have been released at the time of eruption and thus would not be preserved in the trapped glass (Wallace *et al.* 1995). Felsic magmas frequently contain dissolved water in the range of 3–5 wt%, and are capable of producing large-scale explosive eruptions, particularly when associated with caldera-forming events (Rose & Chesner 1987; Gardner *et al.* 1991).

Table 1. *Representative electron microprobe analyses (wt%) of melt inclusions in primary quartz crystals, Cerro Viejo*

Sample	del-1	del-2	del-3	del-4	del-5	del-6	del-7	del-8	del-9	del2-1	del2-2	del2-3	del2-4	arg1-1	arg1-2	arg1-3a	arg5b-1	arg5b-2	arg5b-4	arg5b-6	arg12a-1	arg12a-3	arg7-1	arg7-2	arg3-2
TiO_2	0.17	0.20	0.25	0.15	0.27	0.22	0.13	0.32	0.27	0.24	0.30	0.15	0.29	0.07	0.14	0.04	0.27	0.01	0.12	0.11	0.09	0.17		0.07	0.07
Al_2O_3	11.89	12.18	12.04	11.83	11.95	11.86	12.10	11.75	12.06	11.88	12.03	12.14	12.42	12.50	10.28	10.85	12.14	11.54	12.31	10.24	12.00	11.84	11.44	11.27	11.59
P_2O_5	0.03	0.05	0.03				0.01	0.02	0.06	0.02	0.02		0.03		0.02	0.02	0.18	0.02	0.01	0.01	0.01			0.01	
F			0.01		0.01		0.03			0.03			0.01		0.01						0.03	0.01			
SiO_2	74.81	75.02	74.27	74.13	73.93	74.05	73.93	74.92	74.08	75.26	75.34	74.66	76.21	74.74	73.36	74.41	74.94	73.88	74.65	72.92	76.06	75.56	73.93	73.62	74.51
MnO	0.01	0.08	0.01	0.04	0.02	0.05	0.05	0.07	0.04	0.04	0.05	0.04	0.08	0.02	0.02	0.05	0.01	0.05	0.05	0.02	0.07	0.01	0.03	0.07	0.05
Na_2O	1.76	1.70	1.59	1.76	1.42	1.74	1.77	1.67	1.71	1.63	1.75	1.53	1.36	2.98	4.14	3.39	3.13	3.66	3.57	3.74	3.92	3.51	3.12	3.23	3.38
Cl	0.31	0.29	0.30	0.31	0.28	0.31	0.29	0.26	0.27	0.25	0.25	0.23	0.25	0.11	0.04	0.14		0.05	0.08	0.06	0.10	0.10	0.09	0.08	0.08
FeO	1.93	1.93	1.90	1.64	1.85	1.81	1.86	2.04	1.95	1.98	1.99	1.93	2.02	0.94	0.86	0.82	1.08	0.77	0.73	0.73	0.82	0.89	0.87	0.81	0.79
MgO	0.81	0.89	0.92	0.86	0.77	0.84	0.88	0.82	0.83	0.80	0.83	0.87	0.90	0.22	0.36	0.29	0.54	0.34	0.37	0.32	0.42	0.38	0.23	0.24	0.25
K_2O	2.12	2.17	2.20	2.19	2.24	2.16	2.18	2.17	2.27	2.14	2.16	2.13	1.56	4.41	5.10	4.14	4.18	4.56	4.62	4.63	5.12	4.75	3.76	3.81	4.04
CaO	1.95	1.93	1.92	1.76	1.90	1.96	1.92	1.88	1.96	1.89	1.87	1.95	1.82	0.64	0.66	0.56	1.19	0.75	0.81	0.75	0.75	0.85	0.49	0.53	0.51
Totals	95.78	96.43	95.44	94.66	94.64	95.02	95.14	95.51	95.50	96.14	96.59	95.63	96.95	96.63	94.98	94.71	97.67	95.62	97.33	93.52	99.37	98.07	93.94	93.73	95.26

Data were gathered on an ARL SEMQ microprobe under conditions described in Huff *et al.* (1996).

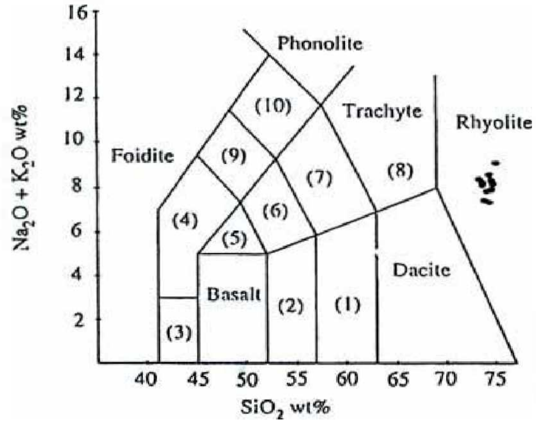

Fig. 9. Quartz-hosted glass melt inclusions from Cerro Viejo were analysed by electron microprobe and the data plotted in anhydrous form on a total alkalis v. silica (TAS) diagram. The high silica content indicates the glass is rhyolitic in composition. Field names are (1) andesite, (2) basaltic andesite, (3) picrobasalt, (4) tephrite, basanite, (5) trachybasalt, (6) basaltic trachyandesite, (7) trachyandesite, (8) trachydacite, (9) phonotephrite, and (10) tephriphonolite.

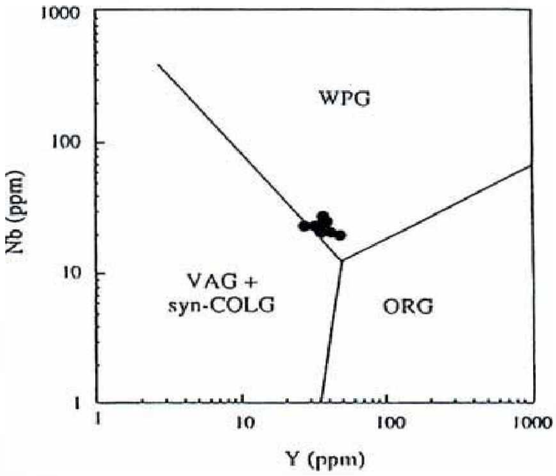

Fig. 11. A tectonic discrimination diagram from Pearce *et al.* (1984) showing the position of the Cerro Viejo volcanic rocks in terms of granitic origins. WPG, within plate granite; ORG, ocean ridge granite; VAG, volcanic arc granite; syn-COLG, syn-collision granite. The samples fall on the boundary between volcanic arc and within plate granites, typical of collision margin felsic volcanic rocks.

Whole-rock major and trace element analyses of selected Precordillera K-bentonites are given in Table 2. Chondrite-normalized rare earth element (REE) plots of five Cerro Viejo samples (Fig. 10) are relatively enriched in light REE and relatively depleted in heavy REE, which is typical of highly evolved, felsic magmas. Moreover, most have a fairly pronounced negative Eu anomaly, characteristic of felsic magmas in which most of the plagioclase has already crystallized. When plotted on the granite tectonic discrimination diagram of Pearce *et al.* (1984), the Cerro Viejo volcanic rocks fall on the boundary between volcanic arc and within plate granites (Fig. 11). Based on comparison with previously-studied K-bentonite beds (Bergström *et al.* 1995; Huff *et al.* 1996; Kolata *et al.* 1996), these appear to represent vitric fallout ash from large-scale explosive volcanism associated with collision-margin tectonism. These data are consistent with the presence of an active Gondwana continental margin in the Early–Mid-Ordovician (Coira *et al.* 1982; Ramos *et al.* 1986; Dalla Salda *et al.* 1992*a*).

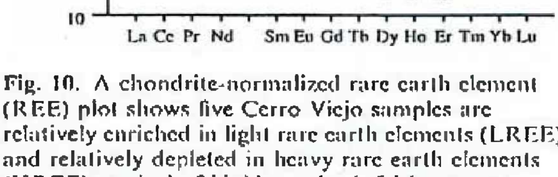

Fig. 10. A chondrite-normalized rare earth element (REE) plot shows five Cerro Viejo samples are relatively enriched in light rare earth elements (LREE) and relatively depleted in heavy rare earth elements (HREE), typical of highly evolved, felsic magmas. Moreover, most have a fairly pronounced negative Eu anomaly, typical of felsic magmas in which most of the plagioclase has already crystallized out taking the Eu with it.

Palaeotectonic setting and volcanic source

An unresolved question concerning the Precordilleran K-bentonites is the location of the volcanoes that produced these ashes. In the case of Quaternary and Holocene ashes, regional mapping combined with geochemical and mineralogical fingerprinting is frequently capable of pinpointing the location of the source vents. However, with ancient volcanic rocks those source vents have generally been destroyed long since and one is confronted with problems similar to most palaeogeographical reconstructions.

Table 2. *Representative whole-rock major (wt%) and trace element (ppm) analyses of K-bentonites*

Sample	ARG1	ARG3	ARG4	ARG5B	ARG6	ARG7	ARG8B	ARG12A	ARG13	ARG14
SiO_2	56.70	50.30	58.50	65.70	45.00	44.40	55.70	52.20	53.20	53.00
Al_2O_3	23.70	27.40	20.60	18.00	25.50	24.00	23.30	23.30	23.80	23.20
Fe_2O_3	1.94	2.33	4.39	2.47	4.51	2.39	2.35	5.16	4.77	4.83
MgO	2.01	2.33	1.51	1.79	2.23	2.15	2.30	1.64	1.69	1.60
CaO	0.07	0.32	0.75	0.51	3.14	5.64	0.10	0.74	0.36	0.32
Na_2O	1.21	0.97	0.60	0.38	0.41	0.29	0.84	1.74	1.31	1.59
K_2O	3.52	3.84	2.24	2.07	3.34	3.10	3.63	2.4	3.32	3.22
TiO_2	0.33	0.31	0.83	0.22	0.47	0.30	0.31	0.58	0.59	0.62
MnO	0.01	0.01	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.02
P_2O_5	0.14	0.06	0.20	0.06	0.04	0.05	0.14	0.27	0.17	0.13
LOI	10.10	11.80	10.10	8.75	15.10	17.70	11.30	11.60	10.70	11.20
AS	27	17	37	5.3	31	16	13	39	290	310
B	240	360	120	160	310	320	250	240	290	340
Ba	3700	5200	3000	2600	4500	4200	4000	3800	4400	5300
Be	3	8	2	2	6	6	3	3	6	4
Bi	0.6	1.1	0.8	1.0	0.5	0.9	0.5	0.5	1.5	1.0
Br	5	4	2	3	4	5	5	3	4	4
Cd	0.6	0.5	0.4	0.8	0.6	0.5	0.8	1.2	0.5	0.4
Cl	2300	300	100	300	300	100	2300	11 500	1600	2500
Co	1	1	18	3	5	2	5	4	6	13
Cr	16	6	15	2	9	7	6	9	20	14
Cs	12.0	18.5	8.6	6.2	24.3	15.7	13.3	6.8	14.4	14.3
Cu	29.2	6.1	40.8	8.7	16.4	3.6	27.6	22.1	28.9	36.4
Ga	25	79	21	16	69	63	24	25	71	77
Ge	10	10	10	10	10	10	10	10	10	10
Hf	13.0	8.4	14.0	7.2	13.0	8.1	11.0	18.0	9.3	7.1
Li	21	37	36	39	48	40	21	31	53	50
Mo	1	9	14	3	11	12	6	4	8	8
Nb	28	14	22	22	23	17	26	20	20	22
Ni	13	8	52	2	16	39	12	17	44	60

Pb	31	6	24	27	27
In	0.5	0.5	0.5	0.5	0.5
Rb	123	145	83	73	136
S	50	0.224	50	50	1.46
Sb	4.0	4.3	3.5	1.1	2.7
Sc	5	9	13	8	10
Se	1	1	1	1	1
Sn	12	50	14	11	50
Sr	190	100	195	145	183
Ta	0.5	2.3	1.6	2.7	1.7
Th	33	46	25	32	34
Tl	1	1.5	2.5	0.4	1.8
U	9.6	10.1	12.4	10.1	8.0
V	36	42	95	5	40
W	1	4	6	1	3
Y	36	32	25	30	56
Zn	160	52	320	82	92
Zr	340	190	410	160	360
La	70.1	14.1	43.9	30.8	38.3
Ce	154.0	30.6	90.7	77.2	22.6
Pr	17.0	3.5	9.6	9.0	9.2
Nd	59.0	11.9	34.2	33.6	32.9
Sm	11.1	2.5	6.5	8.0	6.7
Eu	2.0	3.9	1.7	1.2	4.2
Gd	9.2	3.5	6.0	6.7	8.1
Tb	1.3	0.6	0.8	1.1	1.4
Dy	7.8	4.0	5.0	7.2	7.9
Ho	1.5	0.9	1.0	1.4	1.6
Er	4.8	2.7	3.1	4.3	4.2
Tm	0.7	0.5	0.5	0.7	0.6
Yb	4.8	3.2	3.4	4.4	3.6
Lu	0.71	0.47	0.52	0.67	0.50
SUM	99.7	100.3	99.8	100.0	100.4

Analyses were performed by Instrumental Neutron Activation.

4	33	7	22	19
0.5	0.5	0.5	0.5	0.5
122	121	94	138	126
2.61	50	50	0.102	0.266
3.8	3.7	4.9	9.3	11.0
8	5	7	16	12
1	1	1	1	1
50	14	9	50	50
263	312	308	166	129
2.1	1.6	1.0	2.3	1.3
37	32	24	42	28
1.4	1	0.7	1.8	1.5
9.3	10.7	7.6	12.5	7.8
39	32	49	180	140
6	1	1	14	14
33	38	48	45	39
32	280	200	170	240
200	320	570	270	240
11.1	67.9	106.0	37.3	23.6
23.8	150.0	213.0	73.1	51.4
2.8	16.0	24.0	9.2	5.7
9.7	59.9	84.4	35.3	21.9
2.1	11.9	14.6	6.7	4.7
3.3	2.0	3.3	4.4	4.2
2.9	9.8	12.2	7.6	6.2
0.6	1.5	1.6	1.3	1.1
3.5	8.9	9.3	6.3	5.5
0.8	1.8	1.8	1.2	1.2
2.4	5.4	5.8	3.4	3.0
0.4	0.8	0.9	0.5	0.5
2.6	5.5	5.9	3.6	3.1
0.37	0.81	0.98	0.56	0.47
100.6	100.0	100.0	100.5	100.4

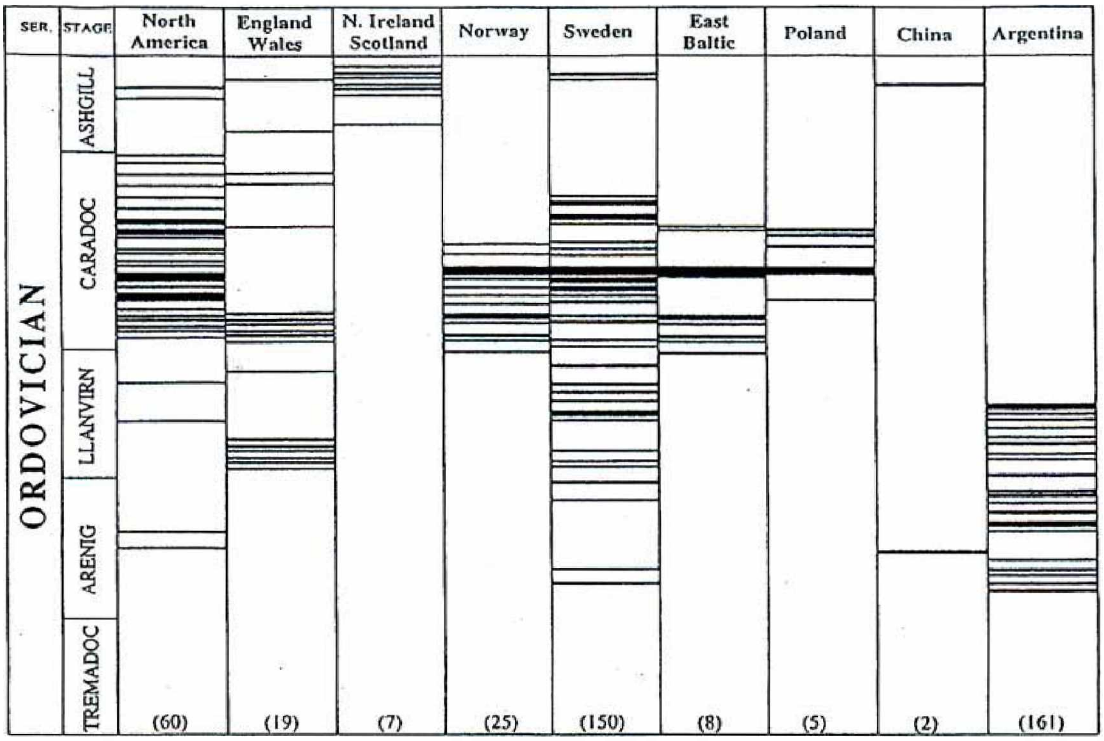

Fig. 12. A comparative global K-bentonite chart for the Ordovician showing principal occurrences and known stratigraphic ranges. Numbers at the bottom of each column indicate the actual number of K-bentonite beds reported from each area. The horizontal lines show the general grouping of beds and also highlight several of the exceptionally thick Caradoc beds that have been regionally correlated.

Assessment of variation in the number of beds, their stratigraphical distribution, and their relative thickness within a region, may provide some clues to the direction of ash transport (Huff *et al.* 1992, 1996; Kolata *et al.* 1996). Such assessment in the Precordillera, however, is complicated by the fact that the K-bentonites occur in thrust belts that were subjected to eastward transport of large but uncertain distance during Andean tectonism. A 50% crustal shortening was estimated along the San Juan River by von Gosen (1992), whereas Allmendinger *et al.* (1982) calculated nearly 95% shortening along the Jáchal River. Moreover, recent work has shown that the top of the San Juan Limestone is of different age at different localities (Hünicken & Sarmiento 1985; Astini *et al.* 1995; Lehnert 1995*a*) Locally, it is marked by a very prominent, largely pre-Silurian, unconformity; hence, the interval in the uppermost San Juan Limestone and the overlying Gualcamayo (or Los Azules) Formation that contains the most numerous K-bentonites may be very poorly, if at all, represented in some sections.

A regional comparison of global Ordovician K-bentonite complexes is shown in Fig. 12 and provides some constraints on the possible juxtaposition of various tectonic plates and plate segments at the time of tephra formation. For example, the abundance and stratigraphical similarity of Caradoc beds in North America and Baltoscandic prompted Huff *et al.* (1992) to propose that these two regions were in close proximity at that time. Haynes *et al.* (1995) challanged the proposed correlation of the Millbrig and Kinnekulle beds on the basis of an apparent dissimilarity in biotite compositions. However, current studies (Huff *et al.* 1997*a*) suggest that the Millbrig beds consist of multiple units, at least one of which is chemically indistinguishable from the Kinnekulle bed. The Argentine sequence, on the other hand, has a different age distribution of K-bentonite beds, and they provide no supporting evidence of a close association between the Precordillera and the other Ordovician sedimentary basins in Fig. 12.

Comparison with North America

More than 60 K-bentonite beds are currently known from the Ordovician of North America (Kolata *et al.* 1996) and some of these beds, such as the Deicke and the Millbrig K-bentonites, are widely distributed. However, a comparison of the stratigraphical distributions of ash beds in the Precordillera and North America (Fig. 13) show considerable differences (Bergström *et al.* 1996). In the latter region, very few ash beds are known from Lower Ordovician and the lower Mid-Ordovician. These include single beds in Mississippi (Thomas 1988; Kolata *et al.* 1996) and in the Marathon area, western Texas (King 1937), an undetermined number of beds of early Mid-Ordovician age in a giant sinkhole near Douglas Lake, eastern Tennessee (Laurence 1944), and a few ash beds in western Newfoundland (Kolata *et al.* 1996). Keller & Dickerson (1996) recently misidentified some calcareous mudstones of early Mid-Ordovician age from the Solitario region, western Texas, as K-bentonites. Hence, we currently know of no obvious counterpart in North America to the extensive K-bentonite bed complex of Early and early Mid-Ordovician age in the Precordillera. However, it may be significant to note that much of the lower Middle Ordovician is not represented in the successions in the Southern and Central Appalachians, where this interval is cut out by the prominent Sauk-Tippecanoe unconformity (Ross *et al.* 1982; Faill 1997).

The principal K-bentonite complex in eastern North America is in the upper Middle Ordovician (Mohawkian) where there are more than 40 ash beds (Bergström *et al.* 1996; Kolata *et al.* 1996), two of which may reach a thickness of 0.1–1 m (Huff *et al.* 1996). No equivalents to this K-bentonite complex, nor to the few North American Upper Ordovician ash beds, are known in the Precordillera. This can be taken as an indication that the close Mid-Ordovician juxtaposition of the Precordillera and easternmost North America shown in several recent paleogeographical reconstructions (Dalla Salda *et al.* 1992*a*; Dalziel *et al.* 1994) is unlikely to be correct. On the other hand, juxtaposition of North America and Baltoscandia is more likely for this time interval, as suggested by Huff *et al.* (1995*b*).

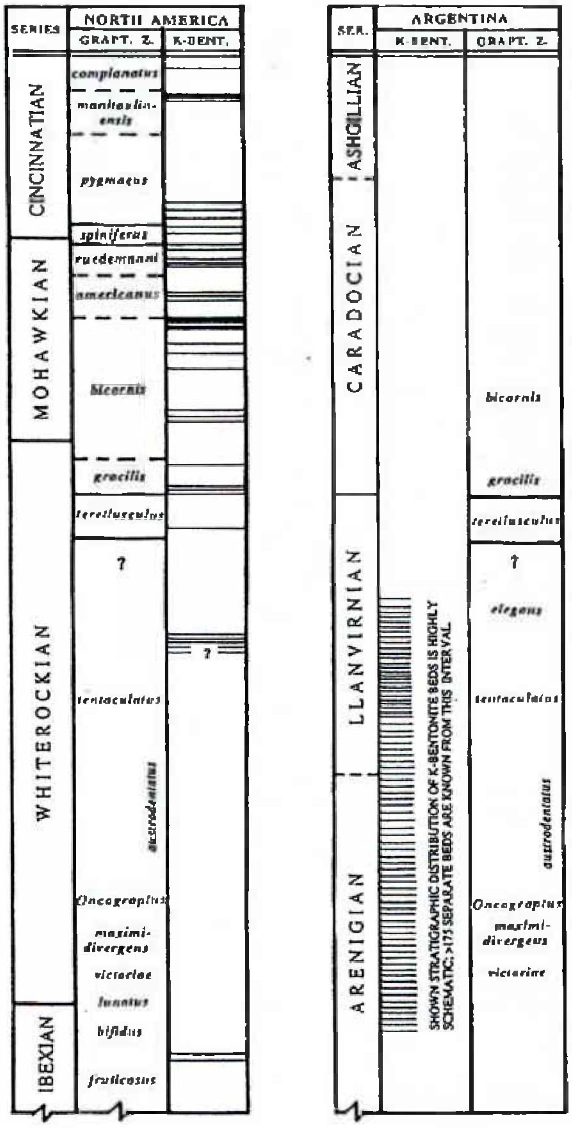

Fig. 13. Chart showing the comparative distribution of K-bentonites in North America and Argentina and associated graptolite zones. The Argentine succession of K-bentonites does not have an identifiable counterpart in North America.

The Famatina magmatic arc

Based on the geochemical characteristics of Precordilleran K-bentonites, the volcanoes from which the ashes erupted developed on continental crust in a convergent tectonic setting, either in the form of an arc situated on the Gondwana margin or as a colliding terrane of continental affinity. Several authors interpret the Eastern Puna–Famatina magmatic belt as an outer magmatic arc (Rapela *et al.* 1992) that was located close to the southwestern Gondwana margin in the south Iapetus Ocean (Dalziel *et al.* 1994). Palaeomagnetic evidence lends support to this hypothesis by placing the Eastern Puna–Famatina belt in the south Iapetus Ocean, close to the Gondwana margin, during Mid-Ordovician time (Conti *et al.* 1996). Palaeobiogeographical arguments (Benedetto & Sánchez 1996) further support an intra-Iapetus positioning for the Famatina Ordovician series. The accretion of this arc to the Gondwana craton was accompanied by the emplacement of a number of granitoid plutons in the Western Sierras Pampeanas. These plutons were loosely identified as pre-Taconic, Taconic, and post-Taconic in age (Lopez de Luchi & Dalla Salda 1995) in reference to the geodynamic model proposed by Dalla Salda *et al.* (1992*b*), which envisaged the Taconic Appalachians and the Famatinian arc as a single orogenic belt. The same plutonic groups had been labelled G1, G2, and G3, respectively, by Rapela *et al.* (1990). The pre-Taconic or G1 group (Late Cambrian–Early Ordovician granitoids, 520–460 Ma) are stocks connected to minor granitic plutons. The Taconic or G2 granitoid group (460–420 Ma) includes plutons concordant to regional foliation, essentially biotite–muscovite peraluminous monzogranites to syenogranites, with minor granodiorites and tonalites associated with an extensive granitic migmatization. The post-Taconic or G3 granitoids (420–360 Ma) are peraluminous to slightly peralkaline and poorer in MgO than the Taconian granitoids. The onset of granitoid emplacement and associated volcanism coincided with the development of sedimentary basins in the northern and central Sierra de Famatina and in the Puna Palaeozoic belt (Coira *et al.* 1982; Koukharsky *et al.* 1988; Coira & Nullo 1989). A more recent evaluation of these ages is provided by Pankhurst *et al.* (this volume). In the Puna (Altiplano) a pyroclastic–sedimentary marine sequence of Arenig to Llanvirn age can be recognized, and geochemical data from these volcaniclastic rocks suggest a continental arc source.

Mannheim (1993) concluded that the geochemical features of the early Palaeozoic rocks in the Sierra de Famatina resulted from two different environments of magma generation. In one case, subduction-related basic primary magmas were generated in an island arc setting, and in the second case, Tremadoc to Llanvirn acidic peraluminous magmas formed during crustal anatexis and produced pyroclastic deposits such as Las Planchadas Formation. Toselli *et al.* (1990) described an episode of Ordovician magmatism and volcanism in which pyroclastic materials (>400 km^2) were derived from acidic to intermediate magmas. This magmatism was synchronous with sedimentation of shallow water rocks of early–mid-Arenig age (Aceñolaza & Toselli 1984; Vaccari *et al.* 1993). Although these Famatinian rocks overlap in age with strata containing K-bentonites in the Guandacol region, they appear to contain no K-bentonites or similar pyroclastic deposits. However, further comparative studies, such as geochemical fingerprinting, precise age dating, and mineralogical investigations, are still needed to clarify many aspects of the tectono-thermal setting and volcanic source of Lower–Middle Ordovician Precordilleran K-bentonites.

Discussion and conclusions

Numerous K-bentonites occur in the San Juan and Gualcamayo Formations in the eastern thrust belts of the Precordillera, and a few ash beds are also known from the central thrust belts. They range in age from the middle Arenig *I. victoriae lunatus* graptolite (*Oe. evae* conodont) Zone to middle Llanvirn age in the *P. elegans* (*P. suecicus*) Zone. As is typical of many Ordovician K-bentonites found elsewhere, they consist of a matrix of illite/smectite mixed-layer clay plus a phenocryst assemblage including biotite, beta-form quartz, alkali and plagioclase feldspars, apatite, and zircon, hornblende, clinopyroxene, titanite, and Fe–Ti oxides. Pristine melt inclusions in quartz crystals are rhyolitic in composition.

The Argentine sequence is unique in its abundance of K-bentonite beds, yet when compared with K-bentonite sequences of similar age elsewhere it provides no supporting evidence of a close association between the Precordillera and other Ordovician sedimentary basins along the Iapetus margin at that time. Palaeogeographical reconstruction for the early Palaeozoic is, at best, a 'weight of evidence' process, in which the more pieces of information there are available, the more solid the arguments for a particular scenario. K-bentonite stratigraphical and geographical distribution patterns can be helpful in this process by providing direct evidence of subduction-related explosive volcanism and the accompanying palaeo-wind directions, as well as the relevant sedimentary conditions and magmatic processes. Based on that record, it is clear that subduction-related volcanism in the Precordillera commenced in the mid-Arenig and continued to the late-Llanvirn, coeval with volcanism in the Sierra de Famatina. It has been proposed that the Ocloyic event of the Famatinian orogeny in South America was a continuation of the Taconic orogeny in North America, based on similarities between Cambrian to early Ordovician carbonate sequences in the Precordillera and those of sections along the Laurentian margin (Dalla Salda *et al.* 1992*b*; Dalziel *et al.* 1994). However, this scenario is not supported by the K-bentonite record: whereas the Precordilleran K-bentonites are Arenig to early Llanvirn in age, those associated with the Taconic orogeny in the Appalachians are of mid-Caradoc age. While the Precordillera may well have had its origins on the Laurentian margin we do not find supporting evidence that it was still there during Mid-Ordovician time (Astini *et al.* 1995; Thomas & Astini 1996). Rather, we find the ash pattern to be more consistent with the palaeogeographical reconstructions of Mac Niocaill *et al.* (1997) who envisage drifting of the Precordillera in fairly close proximity to one or more volcanic arcs with eventual collision along the Andean margin of Gondwana during the Ocloyic orogeny in Mid-Ordovician time. The extensive K-bentonite record in the Guandacol region suggests that the source volcanoes may have been located north or northeast of the Precordillera. Conceivably, the Puna–Famatina terrane could have been one of these volcanic arcs and might have served as one source of the K-bentonite ashes, possibly in concert with active arc magmatism on the Gondwana plate itself.

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