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Cordierite-Spinel Troctolite, a New Magnesium-Rich Lithology from the Lunar Highlands

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A clast of spinel troctolite containing 8 percent cordierite ($Mg_2Al_4Si_5O_{18}$) has been identified among the constituents of Apollo 15 regolith breccia 15295. The cordierite and associated anorthite, forsteritic olivine, and pleonaste spinel represent a new, Mg-rich lunar highlands lithology that formed by metamorphism of an igneous spinel cumulate. The cordierite-forsterite pair in the assemblage is stable at a maximum pressure of 2.5 kilobars, equivalent to a depth of 50 kilometers, or 10 kilometers above the lunar crust-mantle boundary. The occurrence of the clast indicates that spinel cumulates are a more important constituent of the lower lunar crust than has been recognized. The rarity of cordierite-spinel troctolite among lunar rock samples suggests that it is excavated only by large impact events, such as the one that formed the adjacent Imbrium Basin.

RARE SPINEL-BEARING TROCTOLITES and cataclasites among lunar highland samples have provided evidence that spinel cumulate layers occur near or below the lunar crust-mantle boundary. A small white clast of spinel troctolite containing crystals of red spinel and grains of cordierite up to 0.3 mm long (Fig. 1, A and B) was found during an investigation of Apollo 15 regolith breccias. Electron microprobe analyses (Table 1) show that this mineral is essentially pure magnesium-cordierite, with <1 weight percent of FeO and no evidence of H_2O, which generally equals 0.5 to 3.0 weight percent in terrestrial cordierites. The troctolite is composed of 75% plagioclase (anorthite), 11% olivine (forsterite), 8% cordierite, 6% spinel (pleonaste) and <0.5% accessory minerals (Table 2). The accessories include small, sparse grains of magnesium-ilmenite, rutile, troilite, metal, and two minute particles of a calcium-phosphorous–bearing phase (apatite?) that are too small for quantitative analyses. The Ni and Co concentrations ($\leq Ni_{55}Co_{3.7}$) in the metal grains (Table 2) are markedly higher than those that have been measured in metals of either meteoritic or lunar provenance from most lunar rocks and soils, but they are comparable with concentrations reported in metals of certain spinel-bearing lunar rocks of deep-seated origin, including spinel troctolite 67435 (*1*) and dunite 72415 (*2*). The calculated bulk composition shows that the cordierite-spinel troctolite is corundum- and nepheline-normative (Table 3).

The small clast of cordierite-spinel troctolite in sample 15295,101 has a well-crystallized mineral assemblage that has undergone minor in situ cataclasis. Anorthite (An_{93}) occurs in coarse-grained, twinned fragments, <0.9 mm long, that are bordered, in some instances, by finely crushed material of the same composition. Cordierite occurs in equant grains, one of which displays the hexagonal sector twinning characteristic of the mineral (Fig. 1C), and in anhedral grains between other mineral pairs (Fig. 1D). The spinel and olivine also occur in two habits: as large euhedral to subhedral crystals, and as small grains aligned along grain boundaries in the clast and between the clast and breccia matrix. Pleonaste is present as euhedral grains up to 0.25 mm in diameter and also in rows of tiny <0.01-mm crystals (Fig. 1D). Some of the larger pleonaste crystals are lustrous and smooth whereas others have pitted surfaces, suggestive of alteration. However, all of the pleonaste grains, large and small, are unzoned and similar in composition. Forsterite (Fo_{90} to Fo_{92}) occurs in subhedral grains (<0.15 mm) with an optically patchy mosaic texture and in thin stringers along grain boundaries (Fig. 1D). The composition is essentially uniform within grains and from grain to grain.

The significance of the textural relations is uncertain. We believe, for reasons discussed below, that this cordierite-spinel troctolite is a metamorphic assemblage. Two generations of olivine, spinel, and cordierite (ol-sp-crd) grains may be present, consisting of large crystals that formed early, and small, interstitial ones that formed later. Alternatively, the growth patterns may reflect an increasing geometric confinement of the modally subordinate ol-sp-crd assemblage to edges and interstices of the plagioclase grains during a single, extended period of crystallization.

Spinel-bearing troctolites and cataclasites are among the rarer rock types in lunar highland samples. The spinel troctolites

Table 1. Bulk rock and mineral compositions of the cordierite-spinel troctolite clast in weight percent.

Component	Bulk* rock	Cordierite (20)†	Spinel (18)†	Olivine (24)†	Plagioclase (20)†
SiO_2	38.58	50.85	0.02	40.30	45.08
Al_2O_3	29.85	34.26	56.61	0.05	34.34
FeO	3.15	0.84	9.97	8.72	0.02
MgO	13.79	13.34	20.47	50.65	0.05
CaO	12.25	0.05	0.05	0.06	19.34
Na_2O	0.41	0.03	0.00	0.00	0.65
K_2O	0.09	0.49	0.00	0.00	0.12
TiO_2	0.06	0.06	0.11	0.05	0.05
Cr_2O_3	1.62	0.02	12.73	0.03	0.02
MnO	0.03	0.02	0.05	0.10	0.01
P_2O_5	0.17	0.02	0.00	0.03	0.26
Total	100.00	99.98	100.01	99.99	99.94

*Bulk composition calculated from mode (Table 2) and assigning all Fe to FeO. †Numbers in parentheses give number of points analyzed and averaged from six or more grains of each mineral.

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have igneous textures and generally have been considered as cumulate rocks (*1*). The spinel cataclasites are gently to severely crushed and partly mixed with foreign materials so that their original textures have been obscured. These include certain white clasts in Apollo 15 breccia 15445, which were originally classified as peridotites (*3*), and five clasts in Apollo 17 soil samples. When first discovered, these five clasts were described as high-pressure (3 to 7 kbar) assemblages possibly derived from the lunar mantle (*4*). Five of the six known samples of spinel cataclasite consist of anorthite, olivine, spinel, and aluminous orthopyroxene (enstatite). The sixth, in Apollo 17 sample 72435, contains the same assemblage plus a single 0.03-mm inclusion of cordierite (*5*). That minute inclusion in spinel was the only cordierite reported from lunar rocks.

The coexisting magnesium-rich spinel and aluminous-orthopyroxene of the spinel cataclasites are stable at pressures of >2 kbar, equivalent to depths exceeding 40 km in the moon (*6*). However, the cordierite-bearing spinel cataclasite from 72435 is relatively rich in iron (Table 4), which indicates that it was most likely derived from relatively shallow levels and is associated with the ferroan anorthosites rather than the magnesium-rich suite of highland norites, troctolites, and dunites (Fig. 2). Herzberg and Baker concluded that the spinel cataclasite in breccia 72435,8 formed at pressures of <1 kbar in the outer 16 km of the lunar crust (*7*). In contrast, the cordierite-spinel troctolite of 15295,101 is highly enriched in MgO, more so than any other sample of the magnesium-rich suite (Fig. 2). This composition allies it with the high-pressure spinel cataclasites. The cordierite-forsterite pair equilibrates at a maximum pressure of 2.5 kbar, equivalent to a depth of 50 km (*6*), permitting a 0.5 kbar (10 km) overlap with the spinel cataclasites. Thus, the cordierite-spinel troctolite must have originated in the uppermost region where spinel-bearing cumulates occur, or from still shallower levels.

The association ol-sp-crd is uncommon even in terrestrial rocks. It is not known in igneous mafic or ultramafic rocks but occurs

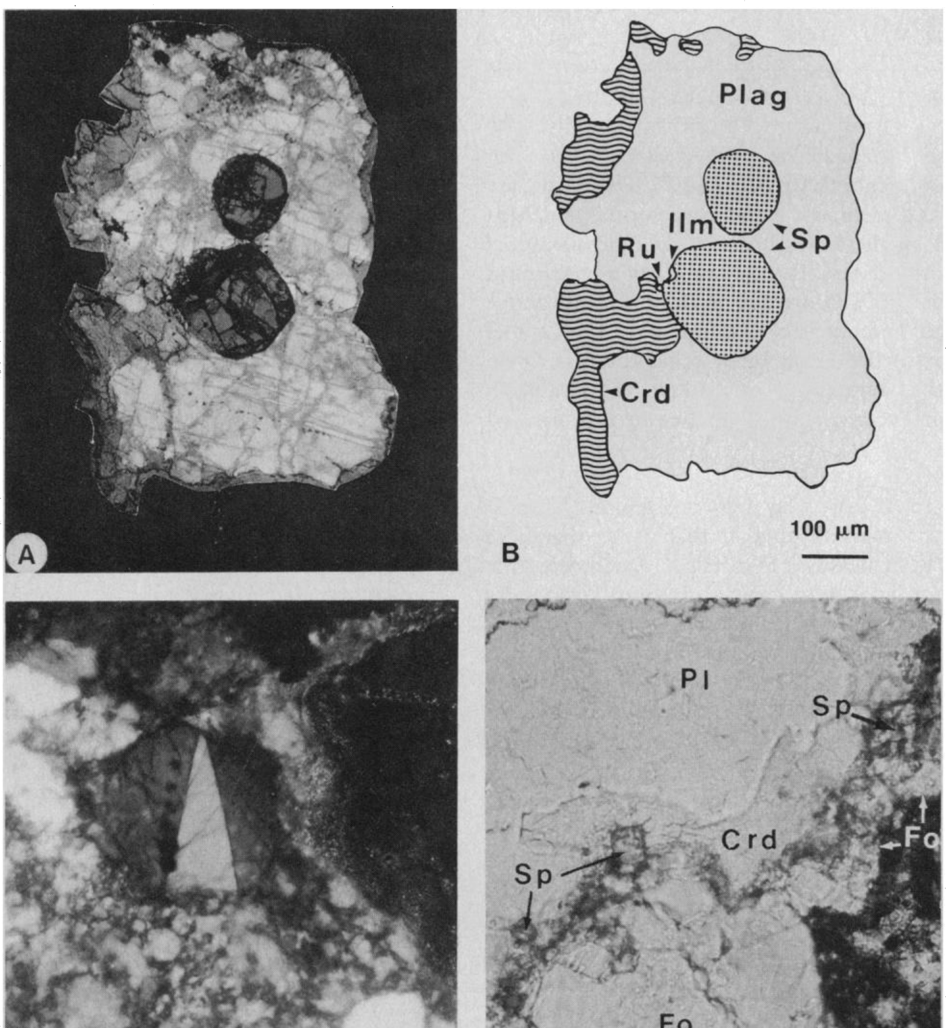

Fig. 1. Some textural relations in the cordierite-spinel troctolite. (**A**) Fragment A, the centermost of 13 fragments into which the clast broke during processing. (Photomicrograph taken in partially cross-polarized light, cut out and mounted on black background to eliminate images of bubbled and discolored epoxy from exposure to electrons during electron microprobe analyses.) (**B**) Sketch map of components in fragment A. Two euhedral crystals of pleonaste spinel (Sp) lie in twinned plagioclase feldspar (Plag). Wavy lines are cordierite (Crd). (**C**) A grain of cordierite with hexagonal sector twinning in fragment E. The crushed material around the grain is also cordierite; white material at left and bottom is anorthite. Dots mark sites of electron microprobe analyses (photomicrograph in cross-polarized light). (**D**) Details of the Fo-Sp-Crd-Pl grain boundaries in fragment M, showing large grains of forsterite (Fo) and plagioclase separated by grains of cordierite, a series of minute spinel crystals, and a thin band of forsterite (photomicrograph in plane polarized light).

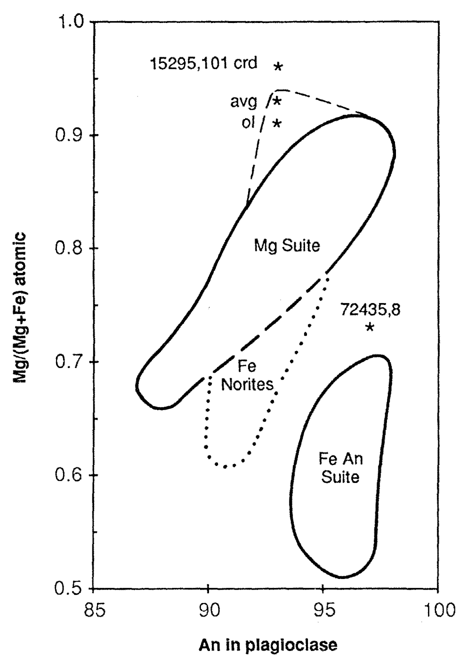

Fig. 2. Positions of the two cordierite-bearing lunar rocks with respect to the ferroan anorthosite suite (Fe An suite) and the magnesium-rich suite (Mg suite) of norites and troctolites of the highlands crust. Points 15295,101 ol, crd, and avg mark the Mg′ values [Mg/(Mg + Fe), atomic] of the forsteritic olivine (0.91), cordierite (0.97), and a weighted average of the two (0.93), plotted against An_{93} in the plagioclase of the cordierite-spinel troctolite. Solid lines outline the compositional range of the Mg and Fe An suites (*13*); dashed lines show the extension of the Mg suite field to include the cordierite-spinel troctolite; dotted lines outline the area occupied by iron norites (Fe norites) (*14*). Point 72435,8 represents the Mg′ value in the olivine (Fo_{73}) versus An_{97} in the plagioclase of the cordierite-bearing spinel cataclasite.

in a contact metamorphic aureole in olivine-chromite ores in the Tara-Misaka ultramafic complex of Japan (*8*). Only a single occurrence of a cordierite-bearing assemblage has been reported in meteorites. It is a 1-mm inclusion consisting of anorthite, spinel, cordierite, aluminous enstatite, sodalite, and a trace of olivine in the Allende carbonaceous chondrite [(*9*) Table 4]. The sodic composition of the Allende assemblage (Table 4) indicates that the meteoritic and lunar cordierites formed in significantly different geochemical environments.

The mineral assemblage of the cordierite-spinel troctolite apparently was in equilibrium. We base this conclusion on the well-crystallized texture of the rock and homogeneity of the mineral compositions. The element partitioning among the cordierite, olivine, and spinel is similar to that in the Tara-Misaka aureole (*8*), and to that among olivine and spinel in lunar spinel cataclasite 15445 (*3*). If the troctolite of 15295,101 is an equilibrium assemblage, it must represent either a recrystallized differentiated magma or a recrystallized igneous cumulate. These two possibilities may be distinguished by examination of liquidus relations in the $CaO-MgO-Al_2O_3-SiO_2$ (CMAS) system (Fig. 3). The inset in Fig. 3 depicts the CMAS tetrahedron, which contains the tholeiite phase volume defined by silica (tridymite) - forsterite - diopside - anorthite (Si - Fo - Di-An). Because of its corundum-normative composition, the cordierite-spinel troctolite lies outside the tholeiite volume, below the An-Fo-Si join and away from the Di apex. The critical question is whether normal lunar magmas that originated in the tholeiite volume could have evolved through the An-Fo-Si join to corundum-normative compositions.

Experimental work on the CMAS system indicates that the An-Fo-Si join is a thermal divide that separates basalts from corundum-normative liquids (*10*). In projection [(*11*) Fig. 3] the join is defined by the Si-Fo tieline with corundum-normative compositions lying to the left, and the tholeiite volume appears as the triangle Si-Fo-Di. A liquid that could produce the cordierite-spinel troctolite of 15295,101 is represented by the corundum-normative peritectic point "α" (where cordierite, spinel, forsterite, anorthite, and liquid are in equilibrium). The only possible access to this peritectic point for tholeiitic liquids is along the Sp-Fo-(An) reaction line. However, even with fractional crystallization, tholeiitic liquids are forced to leave the reaction line before they can ever pass out of the tholeiitic volume (*12*). Thus, the thermal divide effectively prevents the derivation of mineral assemblages such as that of the cordierite-spinel troctolite by the evolution of normal tholeiitic magmas. The rock texture and mineral chemistry bear out this conclusion. The cordierite-spinel troctolite is made up of unzoned minerals, and shows no evidence of late-stage mesostases or other distinctively igneous textures.

The most probable explanation for the assemblage in 15295,101 is that it arose from a multistage process, beginning with the formation of a corundum-normative, spinel-rich cumulate by crystal settling in a mafic or ultramafic magma. If the cumulate formed at pressures <2.5 kbar, subsolidus recrystallization could have produced cordierite in situ. If the pressure were >2.5 kbar, the cumulate would have to have been transported to higher levels in the crust before being metamorphosed and recrystallized to a cordierite-bearing assemblage. As a variation of this theme, cordierite could have crystallized from a partial melt of a corun-

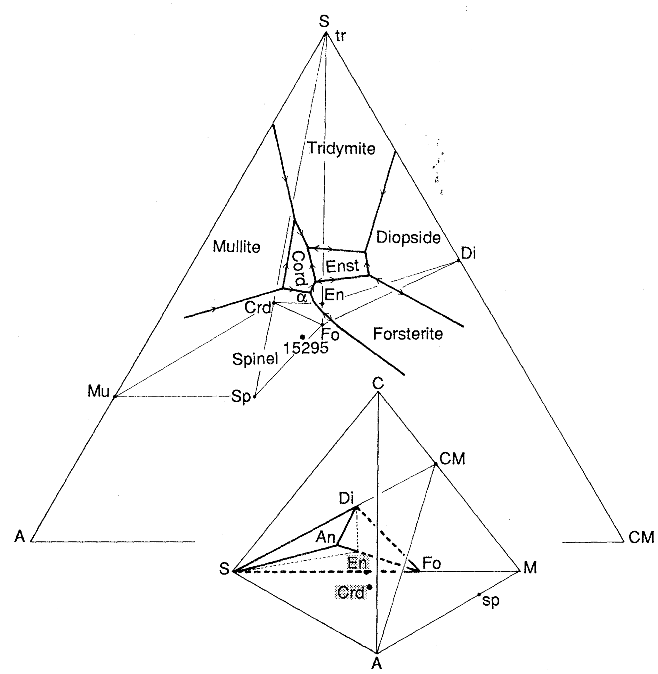

Fig. 3. Liquidus relations in the $CaO-MgO-Al_2O_3-SiO_2$ (CMAS) system at 1 bar as projected from anorthite onto the plane A-S-CM. The inset shows the CMAS tetrahedron with the projection plane shaded, as well as the tholeiite phase volume defined by silica-forsterite-anorthite-diopside (Si-Fo-An-Di). The projected liquidus diagram shows the thermal divide Fo-An-Si as the line Fo-Si, and the tholeiite phase volume as the triangle Si-Fo-Di. Point "α" represents a corundum-normative peritectic that would produce a cordierite-bearing spinel troctolite from a tholeiitic liquid. Point 15295 is the projected composition of the cordierite-spinel troctolite; [from (*13*)]. Cord and Enst are the primary liquidus fields of cordierite and enstatite (En).

Table 2. Mode and average mineral compositions; An, anorthite; Ab, albite; Or, orthoclase; Fo, forsterite; tr, trace.

Phase	Composition
75% Plagioclase	$An_{92-94}Ab_{5-7}Or_{0.5-1.3}$
11% Olivine	Fo_{90-92}
8% Cordierite	$Mg_2Al_4Si_5O_{18}$
6% Spinel	$(Mg_{0.78}Fe_{0.22})(Al_{0.87}Cr_{0.13})_2O_4$
tr Mg-ilmenite	$(Mg_{0.36}Fe_{0.64})TiO_3$
Rutile	TiO_2 (Nb, Zr not detected)
Troilite	FeS
Metal	$(Fe_{43-45}Ni_{53-55}Co_{1.3-1.65})$, $(Fe_{45-47}Ni_{49-52}Co_{2.5-3.7})$

Table 3. CIPW norm in weight percent, calculated from bulk composition (Table 1).

Olivine	27.42
Nepheline	1.40
Anorthite	59.66
Albite	0.89
Orthoclase	0.53
Corundum	7.21
Ilmenite	0.11
Chromite	2.39
Apatite	0.39
Total	100.00

Table 4. Extraterrestrial cordierite-bearing rocks in modal percent except for Allende meteorite (mode not published); SP, spinel; Fo, forsterite; An, anorthite; Crd, cordierite; tr, trace.

Apollo 15 15295, 101 Crd-Sp troctolite	Apollo 17 72435 (*5*) Sp cataclasite	Meteorite Allende (*9*) Crd nodule 0.5 mm
75% An_{93}	74% An_{94-98}	An_{90} inclusion
11% Fo_{91}	20% Fo_{73}	Fo_{96} trace in rim
8% Cordierite	tr Crd (4% FeO)	Crd (4% Na_2O)
6% Sp pleonaste	5% Sp pleonaste	Spinel inclusion
	1% Al-enstatite	Al-enstatite inclusion
		Sodalite [$Na_4(AlSiO_4)_3Cl$] in rim

dum-normative spinel cumulate.

In conclusion, we postulate that metamorphic recrystallization of a spinel-rich igneous cumulate at a maximum pressure of 2.5 kbar and depth of 50 km in the lunar crust produced the cordierite-spinel troctolite. As the crust-mantle boundary is at a depth of 60 km and the magnesium-rich suite probably is the most abundant crustal material at depths greater than about 30 km, the rock must have originated at a depth of 30 to 50 km. At such levels, spinel cumulates may well be more important components of the lunar crust than has been recognized. The rarity of cordierite-spinel troctolite indicates that it forms from spinel-rich precursors at horizons sufficiently deep to be unroofed only in major impact events. We suggest that the clast of cordierite-spinel troctolite was excavated from the adjacent Imbrium Basin.

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Molecular Modeling of the HIV-1 Protease and Its Substrate Binding Site

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The human immunodeficiency virus (HIV-1) encodes a protease that is essential for viral replication and is a member of the aspartic protease family. The recently determined three-dimensional structure of the related protease from Rous sarcoma virus has been used to model the smaller HIV-1 dimer. The active site has been analyzed by comparison to the structure of the aspartic protease, rhizopuspepsin, complexed with a peptide inhibitor. The HIV-1 protease is predicted to interact with seven residues of the protein substrate. This information can be used to design protease inhibitors and possible antiviral drugs.

THE LIFE CYCLE OF RETROVIRUSES such as HIV, the pathogen of AIDS, requires a specific protease (PR) that processes the precursor *gag* and *pol* polyproteins into mature virion components (*1–3*). If the PR is absent or inactive, noninfectious virus particles with aberrant structure are produced (*4*). Therefore, specific inhibitors of retroviral proteases are potential therapeutic agents for blocking HIV infection. However, rational drug design requires detailed knowledge of the three-dimensional structure of the target. Recently we solved the crystal structure of the PR from Rous sarcoma virus (RSV), Prague-C strain (*5*). We have used this structure to construct a model of HIV-1 PR and present details of the proposed substrate-binding site of the HIV-1 enzyme.

All of the retroviral proteases contain a triplet, Asp-Thr/Ser-Gly, which, together with known biochemical properties of these enzymes, indicates that they are members of the aspartic protease family (*6–8*). This relation was confirmed by the three-dimensional structure of the RSV PR (*5*), which has now been refined to an *R*-factor of 0.16 with 2 Å x-ray data. Two PR subunits interact to form a symmetric dimer with an active site that is similar to the highly conserved active sites of monomeric cellular proteases such as pepsin (*9*), rhizopuspepsin (*10*), and endothiapepsin (*11*). The root-mean-square (rms) deviation in the positions of 36 superimposed Cα atoms near the active site is about 2 Å between rhizopuspepsin (*10*) and the RSV PR dimer (*5*). There are also considerable similarities in the overall shape of the two molecules. For 170 Cα atoms aligned in both structures (out of 232 placed in the current RSV PR model), the total rms deviation is only 3.2 Å (*12*). Retroviral proteases, however, are simpler than the cell-derived pepsin-like proteins. The dimer of the retroviral PR consists of 200 to 250 amino acids, whereas a single molecule of a cellular protease is about 325 amino acids long and exhibits intramolecular quasi-symmetry. The structural elements of cellular aspartic proteases are conserved

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       ------a------       ----------b----------             -------
       1                 10                  20                  30
RSV    L A M T M E H K D R P L V R V I L T N T G S H P V K Q R S V Y
           1                 10
HIV-1      P Q I T L W Q R P L V T I K I G                     G Q L

      --c----------      -----d----- ---h---         -------a'------
                       40                  50                  60
RSV    I T A L L D S G A D I T I I S E E D W P T D W P V M E A A N P
       20                  30                  40
HIV-1  K E A L L D T G A D D T V L E E M S L P G R W K P K M I G
                 * * *

       "flap"          ------------------b'-----------------  -------
                     70                  80                  90
RSV    Q I H G I G G G I P M R K S R D M I E L G V I N R D G S L E R
               50                    60
HIV-1        G I G G F I K V R Q Y   D Q I L I E I C             G H
       . . . . . . . .

       ----c'------------      ---d'---  -------h'------ ----q-----
                   100                 110                 120
RSV    P L L L F P A V A M V R G S I L G R D C L Q G L G L R L T N L
       70                  80                  90                99
HIV-1  K A I G T V L V G P T P V N I I G R N L L T Q I G C T L N F
                                       * * *
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Fig. 1. Amino acid sequence alignment for the proteases from HIV-1 and RSV (*22*). The secondary structural elements of the RSV PR are indicated on top of the amino acid sequences and are labeled according to the scheme proposed by Blundell *et al.* (*11*). A one-turn α helix is labeled *h* helix, and a longer α helix is labeled *h'*. The flexible flap lies between β strands *a'* and *b'*, and residues 63 to 70 were not visible in the electron density map for RSV PR (dotted line). This alignment conserves the topology, so that deletions are positioned in surface loops of the three-dimensional structure. The active-site triad Asp-Thr/Ser-Gly is indicated by asterisks, as is the conserved triplet Gly-Arg-Asp/Asn at the start of helix *h'*. The flap region was aligned based on the rules proposed by Andreeva (*23*).

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